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INFRARED SPECTROSCOPIC STUDY OF GAS-SOLID INTERACTIONS

FINAL REPORT

APRIL 1970

Process Control Engineering Division
National Air Pollution Control Administration
Consumer Protection and Environmental Health Services
Public Health Service
U. S. Department of Health, Education and Welfare

Contract No. CPA 22-69-59

Submitted by

General Technologies Corporation
A Subsidiary of Cities Service Company
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by

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16. Abstracts: The aim was to apply infrared spectroscopic methods to handle large numbers of process control samples and to obtain kinetic information to evaluate the effects of variables such as sulfur dioxide concentration on overall process efficiencies and to understand the deadburning phenomenon associated with limestone processes for removal of sulfur dioxide from flue gases. Major effort was directed toward development of rapid reliable methods for analysis of reacted limestones. A solvent system, suitable for dissolving limestone and capable of being made infrared inactive by the dual cell technique was developed. The system--tetrasodium EDTA (ethylenediaminetetraacetic acid) saturated water was found to be the only one of a large number of systems investigated capable of dissolving limestone. Special infrared liquid cells 3 microns thick were developed. The feasibility was studied of using a D_2O based solvent system to determine the oxide and hydroxide contents of reacted limestones. The KBr pellet technique, with and without use of an internal standard was studied in considerable detail. Ion exchange resin techniques were also studied in conjunction with the KBr method. Infrared spectroscopic techniques were also applied to studies of gas-solid interactions between the sulfur dioxide content of a (over)

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Reaction kinetics
Solvents
EDTA
Infrared equipment
Calibrating
Concentration (composition)
pH
Feasibility
Heavy water
Potassium bromide
Ion exchange resins
Sulfates
Hydroxides
Carbonates
Silicon oxides
Roasting
Temperature
Hydration
Magnesium oxides
Dolomite (rock)
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simulated flue gas and various limestone absorbents and to an investigation of the dead-burning phenomenon. The latter has revealed the strong possibility of chemical reactions with silicate impurities during high temperature calcination. Electron microprobe data has revealed that at lower calcination temperature, all of the silicates are present in discrete phases in the limestones. With increasing calcination temperature, silicates were found to diffuse throughout the material. Studies were also performed to confirm the hydration of MgO in calcined, slaked dolomitic materials.

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ABSTRACT

This report constitutes work conducted during the second year of effort to study gas-solid interactions by infrared techniques. A report on the first year's work has been published by the Clearinghouse for Federal Scientific and Technical Information under Public Health Service Number PB 182-988.

The major effort in this investigation has been directed toward development of rapid reliable methods for analysis of reacted limestones. A solvent system, suitable for dissolving limestone and capable of being made infrared inactive by the dual cell technique was developed ~~during this contract.~~ The system—tetrasodium EDTA (ethylenediaminetetraacetic acid) saturated water was found to be the only one of a large number of systems investigated capable of dissolving limestone. Of the many organic systems studied, only solvents containing OH groups, which would dissolve EDTA were of any use. The aqueous solution was found to be best in that limestone solubility from it was highest.

To use such a system for infrared studies, special infrared liquid cells 3 microns thick ~~had to be~~ developed. Using these cells and the new solvent system, calibration curves were obtained for various concentrations of carbonate and sulfate and a number of limestone samples were analyzed for sulfate content. The analysis results compared favorably with values obtained by wet chemical methods and a detailed error analysis of the new method revealed the importance of solution pH as a variable in the analysis. Dissolution of limestone into the saturated tetrasodium EDTA solutions generally caused an increase in pH, the amount of which depended on the amount of sample dissolved and its unreacted oxide content.

Utilizing the thin infrared cells, studies were also made of the feasibility of using a D_2O based solvent system to determine the oxide and hydroxide contents of reacted limestones. From the results obtained, such a procedure does appear to have promise.

A number of other infrared analytical techniques were also investigated under this contract. The KBr pellet technique, with and without use of an internal standard was studied in considerable detail. It was found that these methods yielded results which were subject to considerable variation in accuracy and precision. Ion exchange resin techniques were also studied in conjunction with the KBr method. With this approach, reliable results were obtained for sulfate analysis but analyses for hydroxide and carbonate proved impossible on a reproducible basis.

Infrared spectroscopic techniques were also applied to studies of gas-solid interactions between the sulfur dioxide content of a simulated flue gas and various limestone absorbents and to an investigation of the deadburning phenomenon. In situ spectroscopic studies have been conducted in a high temperature infrared cell in the 375-475°C range and kinetic data has been obtained on two of the individual steps for the overall process reaction. It has been found that at elevated temperatures the absorption reaction:

$$CaO + SO_2 \longrightarrow CaSO_3,$$

with an activation energy of 13.8 Kcal/mole is rate determining. At lower temperature, the oxidation process yielding sulfate, with an activation energy of 41.9 Kcal/mole becomes rate controlling.

Investigations into the mechanisms of deadburning have revealed the strong possibility of chemical reactions with silicate impurities during high temperature calcination. Indeed, shifts in position and changes in intensity with rising calcination temperature have been noted for the Si-O stretches due to silicate impurities in three series of limestones examined. Electron microprobe data has revealed that at lower calcination temperature, all of the silicates are present in discrete phases in the limestones. With increasing calcination temperature, silicates were found to diffuse throughout the material.

Studies were also performed ~~during this contract~~ to confirm the hydration of MgO in calcined, slaked dolomitic materials.

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SECTION I

INTRODUCTION AND SUMMARY

The removal of sulfur dioxide from power plant flue gases has recently become a subject of considerable concern. Several processes have been proposed to satisfactorily remove this pollutant by converting it into either saleable or non-toxic, easily discardable, products. Two potentially economical methods, which result primarily in formation of non-toxic discardable calcium sulfate, are the wet and dry limestone scrubbing processes.

For these techniques to be adequately studied, several problems must first be solved. New analyses which are sufficiently rapid so as to be able to handle large numbers of process control samples must be developed. The classical wet chemical techniques already in use are simply too time consuming if a number of reacted limestone constituents must be determined on a routine basis. Also, kinetic information must be obtained so as to be able to evaluate the effects of variables such as sulfur dioxide concentration on overall process efficiencies and existing problems, such as the deadburning phenomenon, must be understood and overcome.

The aim of this program has been to utilize infrared spectroscopic methods to identify and solve some of the above problems. Specifically, three areas have been studied in considerable detail:

1. Much effort has been directed, during this study, to the development of a rapid, accurate infrared method for the routine analysis of the constituents of reacted limestone.

2. The kinetics of the overall reaction between oxygen, sulfur dioxide and calcined limestone were investigated in considerable detail in the 357-473°C range.

3. A study was made of the possible influences of silicate impurities in the deadburning (i.e. loss of reactivity) of limestone as a function of calcination conditions and the hydration of MgO in slaked calcined dolomitic materials was confirmed.

For the first task to develop rapid, accurate infrared analytical techniques for limestone, a number of techniques were studied in considerable detail. The KBr pellet method, with and without the use of an internal standard was investigated as a technique for rapid analysis. It was found that the calibration curves obtained for sulfate, carbonate, silicate and hydroxide contained considerable scatter and that sulfate analyses run on a number of samples gave results of, in general, poor reproducibility and accuracy. Attempts were made to improve the KBr pellet method by using it in conjunction with standard freeze drying ion exchange techniques. While reproducible and fairly accurate sulfate analyses were found to result from this, useable calibration curves could not be readily obtained for either carbonate or hydroxide, thus limiting the usefulness of this approach to sulfate analysis.

The use of a solution infrared method which would provide a reliable limestone analysis was therefore investigated. With this method, a solution of limestone would be placed in the sample beam of the spectrometer. A cell of equal thickness filled with only the solvent would be used in the reference beam. In order to develop such a method, the first step was the selection of a suitable limestone solvent. Of the many solvent systems investigated, only tetrasodium EDTA (ethylenediaminetetraacetic acid) saturated water[1] was found to effectively dissolve lime and limestone in sufficient amounts to be useful.

An aqueous solvent, however, presented the problem of developing infrared cells suitable for such work. Water, in thicknesses of greater than 10 microns is almost totally absorbing in most of the infrared region[2] and the thinnest commercially available cells are about 7 microns in thickness. In past quantitative studies with aqueous solutions, thin film cells were prepared by deposition of a film of cellulose acetate from acetone solution onto the edges of flat salt plates[3]. However, while such an approach is excellent for preparing single cells, it is useless for making a matched pair of cells. The thin film cells used in our studies were prepared by deposition of a 3 micron silver film onto the surfaces of flat silver chloride plates.

Using a matched pair of such cells, calibration curves were obtained for sulfate and carbonate dissolved in saturated tetrasodium EDTA solution and a number of limestones were analyzed for their sulfate contents. The results agreed well with those obtained from classical wet chemical methods of analysis. A detailed error analysis performed on the data obtained with about one dozen different limestones revealed the importance of solution pH as a variable influencing accuracy of the results.

For the second task kinetic studies were conducted in the 375-475°C range using a high temperature dual cell arrangement to minimize interference from emissions problems that have been encountered in earlier work[4]. In these studies, with both cell compartments maintained at the same temperature, the oxidation and absorption of SO_2 on limestone were studied in detail. Separate series of kinetic experiments, with and without oxygen present in the gas phase, were performed to measure the absorption of SO_2 and the formation of sulfate. The data collected was obtained by two techniques; monitoring of a fixed frequency (1110 cm^{-1} for sulfate and 900 cm^{-1} for sulfite) and scanning of the 1300-700 cm^{-1} region at regular intervals. Both sets of data proved to be in reasonable agreement with each other. From the sulfate formation rate data, an activation energy of 41.9 Kcal/mole was computed for the reaction:

$$CaSO_3 + 1/2O_2 \longrightarrow CaSO_4 \qquad (1)$$

From the 900 cm^{-1} data, a value of 13.8 Kcal/mole was found for the SO_2 absorption step:

$$CaO + SO_2 \longrightarrow CaSO_3 \qquad (2)$$

From further calculations of pre-exponential factors, it was then demonstrated that at temperatures above 500°C, the absorption step is the overall rate determining reaction for

the dry limestone process. Below 500°C, the formation of sulfate via reaction I becomes rate controlling.

For the third task, studies were made in some detail of the possible role silicates may have in the deactivation of limestone (deadburning) during high temperature calcination. Specifically, three series of limestone materials were studied. Spectra were run by the KBr pellet technique of these materials prepared at various calcination temperature. Analysis of all the spectra obtained revealed changes in intensity and band positions for the Si-O stretching bands due to silicate impurities present. This confirms earlier preliminary work(4) in which similar band shifts were reported. Aside from the changes in the silicate bands, no other significant differences in infrared spectra between high and low temperature calcines of the same materials could be noted. Thus, the differences in infrared spectra have been interpreted in terms of chemical reactions between the silica and/or silicates present and the calcined limestone. Studies using the electron microprobe have found that in the low temperature calcines, essentially all of the silicates are contained in discrete phases within the limestone particles. For the higher temperature calcines, some silicates were found in all phases of the materials.

An investigation aimed at confirming the hydration of magnesium oxide in calcined, slaked dolomitic materials was also conducted. It was shown that in these unreacted materials, hydration, indeed, does occur. It was further demonstrated that, upon reaction with flue gas at 750°C, the hydrated MgO either decomposes or reacts preferentially with some gas constituent.

SECTION II

EXPERIMENTAL RESULTS AND DISCUSSION

The work performed under this contract was aimed at the solution of three discrete sets of problems:

1. Analytical investigations,

2. Studies of deadburning and MgO hydration and,

3. High temperature kinetic studies.

In this report, each of these areas will be treated, in whole, in a separate section. This, it is felt, will yield a more easily understandable presentation.

A. ANALYTICAL STUDIES

1. Introduction

One of the aims of this program has been to develop infrared methods for rapid analysis of the constituents of reacted limestones. Two types of analytical methods were investigated in considerable detail. The first was the pressed pellet method and the second was the solvent technique. In studying application of the KBr technique, investigations were also made of application of freeze drying and ion exchange techniques in an effort to gain greater accuracy. Investigations of the solvent approach centered around the choice of a satisfactory limestone solvent and the design and use of an infrared cell system compatible with the solvent chosen.

In this portion of the report, the pellet and solvent technique studies will be treated completely in separate sections for ease of reading.

2. Pellet Technique Studies

(a) Experimental Procedures

For studies using the KBr pellet method, the following general procedures were employed:

Pellets containing from 0.01 to 1.0 weight percent of the desired material were prepared by grinding the appropriate amount of this material together with potassium bromide in the Wig-L-Bug for from 30 to 60 seconds. The KBr pellets were then prepared by pressing the samples in an evacuable die by applying a pressure of 2700 pounds for two minutes. The infrared spectra of the pellets were recorded using a beam attenuator in the reference beam to adjust the 100% base line and calibration curves

were constructed for the various species of interest by plotting the absorbances at specific frequencies versus concentration of that species. For all of this work, the Beckman IR 10 Infrared Spectrophotometer was used.

In some studies using the pellet method, a pure KBr disk was used in the reference beam in place of the attenuator. It may be noted that this approach did not yield any significant improvement in the results.

For studies using an internal standard, the above approach was modified by incorporating a known weighed amount of internal standard along with the material of interest into the KBr pellets. The internal standard used was lead thiocyanate. In the application of this technique, the internal standard was prepared by adding 0.23% by weight of lead thiocyanate (preground for 10 minutes in the Wig-L-Bug) to 4.9327 grams of KBr which had been dried at 120°C. This mixture was then carefully mixed and ground in aliquots and then stored in a dessicator over phosphorous pentoxide prior to use. In preparing calibration plots with the internal standard technique, correlations were made between the ratio of the absorbance at one frequency of the species of interest to the absorbance of the thiocyanate bands with the concentration of the desired species in the KBr pellets.

To obtain a more mixture of samples in KBr, the use of freeze-drying techniques were employed in some investigations. The basic design of the cells used are shown in Figure 1. They consisted of 12/30 and 24/40 standard taper glass joints and a four millimeter bore stopcock. For the freeze drying experiments, the solutions were frozen using a dry ice acetone mixture and the water removed under vacuo, leaving a dried uniform mixture which could be pelletized. Infrared spectra of the samples were measured in the usual manner.

Two variations of the freeze drying technique were investigated. In the first technique, a standard calcium sulfate solution was prepared by dissolving a known amount of this material in the minimum amount of 1M hydrochloric acid and diluting the solution to 100 milliliters. Aliquots of this solution were mixed with a standard solution containing 0.03323 gram of potassium bromide and 0.000054 gram of potassium azide per milliliter. The potassium azide was added for use as an internal standard. The mixtures were frozen using both a dry ice acetone bath and liquid nitrogen. The water was removed under vacuum leaving the resultant mixture in the form of a powder. This powder was then dried in an oven at 120°C for approximately two hours and potassium bromide pellets were prepared after grinding the mixtures for 15 - 30 seconds in the Wig-L-Bug.

The second technique consisted of using ion-exchange resins to dissolve the calcium sulfate. A number of resins in the Na^+, K^+ and H^+ forms were utilized in these studies. Problems encountered with these materials will be treated in a later section of this report.

After suitable calibration curves for sulfate had been obtained with this technique, various limestone samples were analyzed for sulfate content using the

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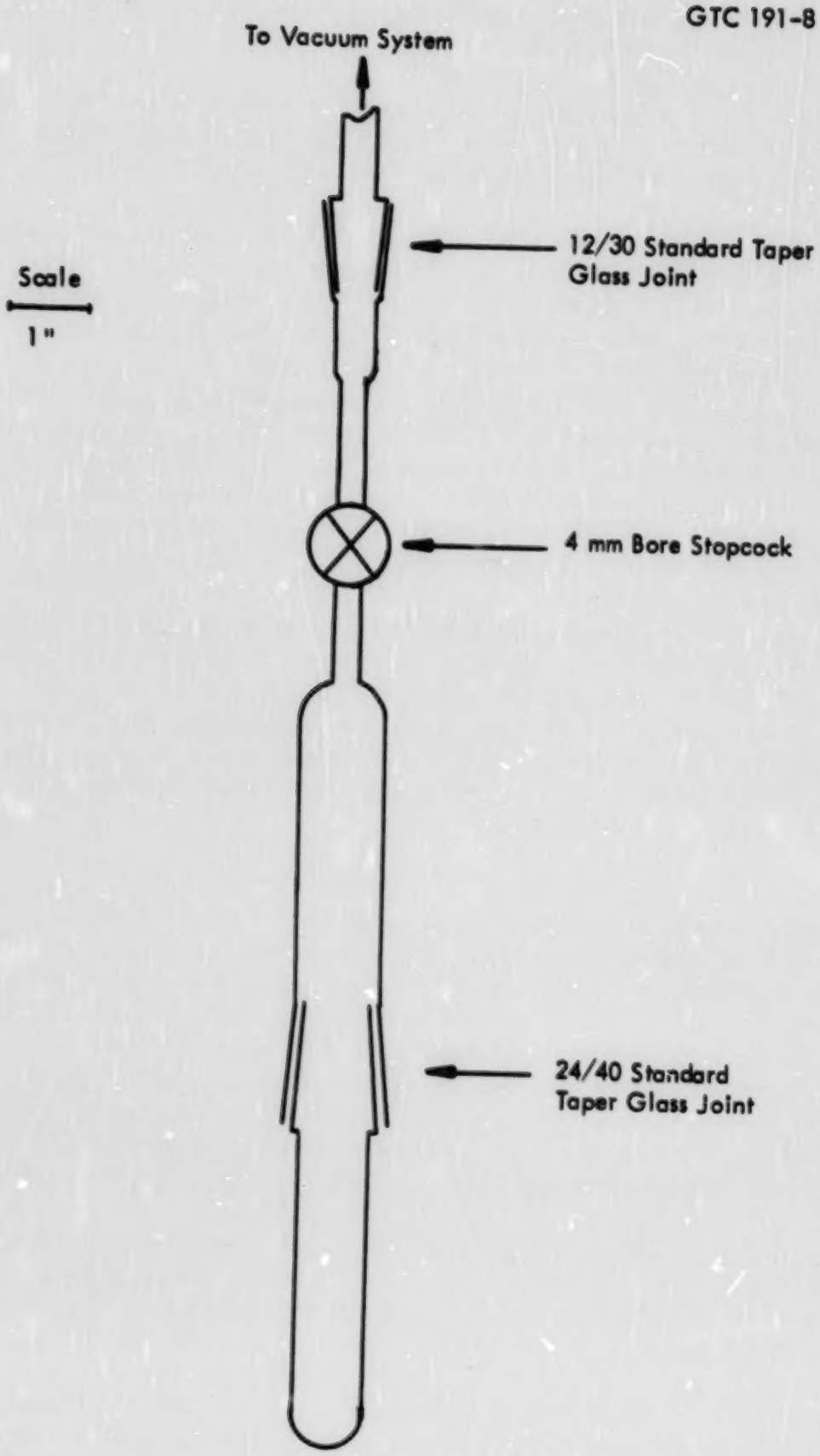

Figure 1. Freeze-Drying Cell

above procedures for sample preparation.

(b) Pellet Studies - Results and Discussion

(1) Application of the KBr Technique to the Quantitative Analysis of Sulfate

The application of the KBr technique to the quantitative analysis of limestone samples can be best understood by considering the Beer-Lambert Law given in Equation 3.

$$A = \alpha c \ell \qquad (3)$$

where A is the absorbance. In $\left(\frac{I_0}{I}\right)$, α is the absorption coefficient, c is the concentration of calcium sulfate in terms of weight percent in potassium bromide and ℓ is the path length of infrared radiation through the pellet (thickness of the pellet in mm). For a particular substance, for example, calcium sulfate, the absorption coefficient should be constant and the absorbance depends upon the concentration of the absorbing species and the path length of infrared radiation through the sample. The standard calibration plot is shown in Figure 2 for the 1158 cm^{-1} band of calcium sulfate and the standard calibration plot using the 678 cm^{-1} band of calcium sulfate is shown in Figure 3. In both of these plots, the best least square fit line is shown along with the experimental points.

In order to check the accuracy of this technique for the quantitative analysis of sulfate, the absorptivity of the 1158 cm^{-1} and 678 cm^{-1} sulfate absorption bands were calculated for each of the KBr pellets containing the sample. The absorptivity is given by Equation 4.

$$k = \frac{A}{c\ell} \qquad (4)$$

where k = absorptivity
A = baseline absorbance
c = concentration in weight percent
ℓ = thickness of the KBr disc in millimeters.

For each pellet, the value of k should be constant. However, results showed there was a deviation in the value of k for both the 1158 cm^{-1} and 678 cm^{-1} absorption bands. The percent coefficient of variation of the mean was 6.7% for the 1158 cm^{-1} absorption band and 8% for the 678 cm^{-1} absorption band. The amount of scattering of points is also indicated in the standard curves for these absorption bands.

Standard calibration curves of calcium sulfate in potassium bromide were also prepared by correcting the absorbance against a pellet containing pure potassium bromide which was placed in the reference beam of the spectrophotometer in place of the beam attenuator. The absorbance of the sulfate band was corrected multiplying it by the factor:

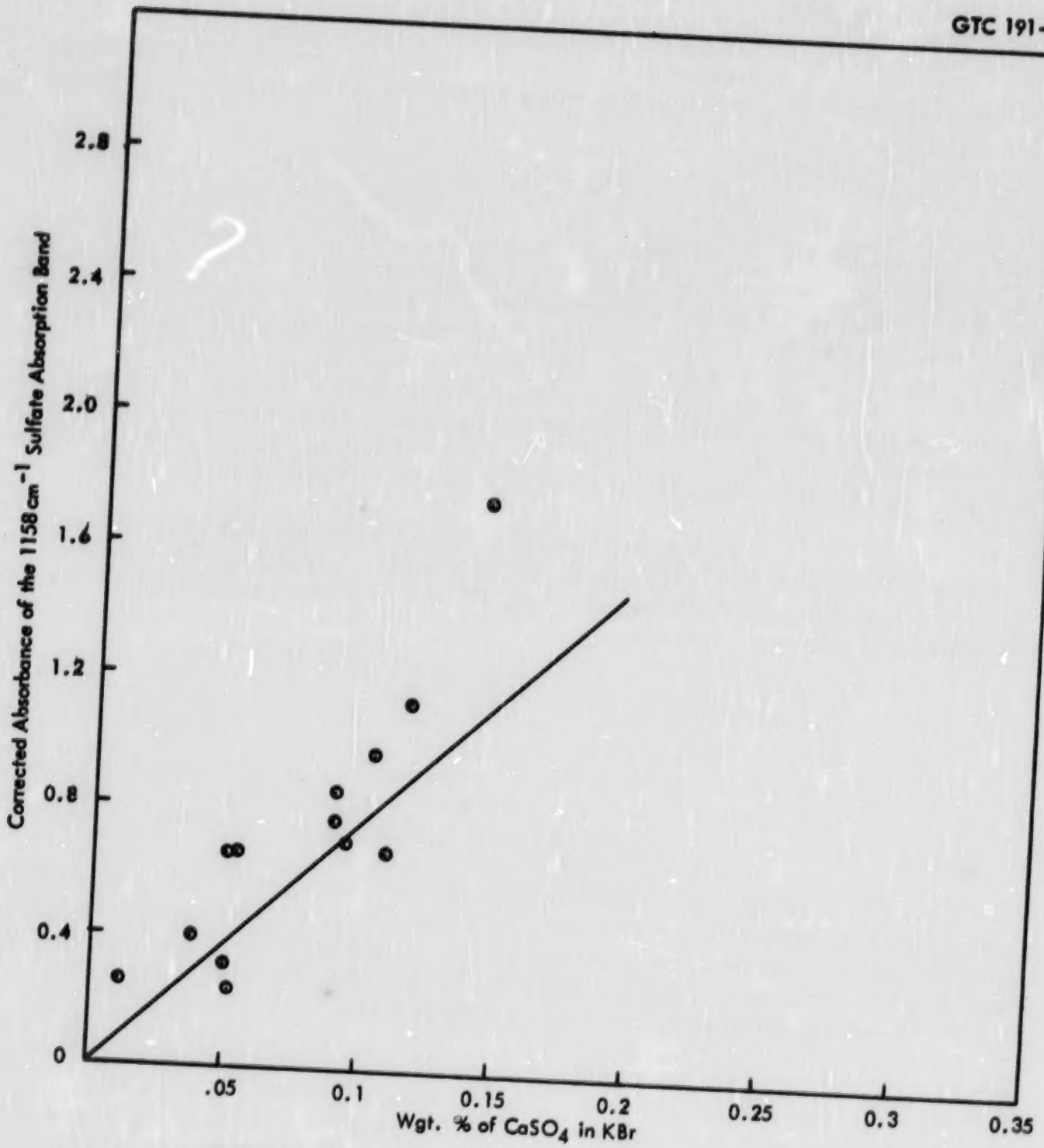

Figure 2. Plot of Corrected Absorbance of 1158 cm^{-1} Sulfate Absorption Band Versus Wgt. % of $CaSO_4$ in KBr

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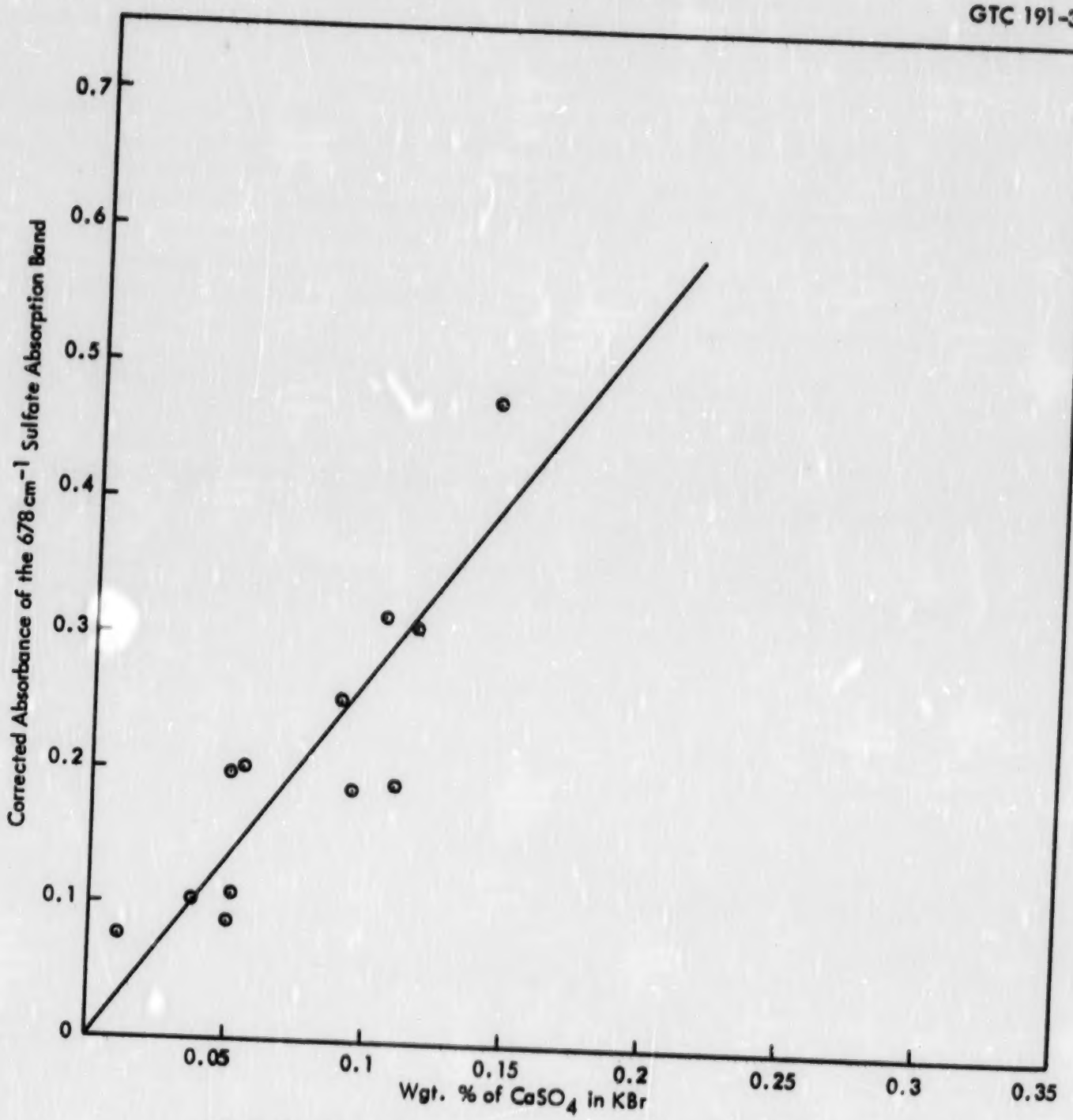


Figure 3. Plot of Corrected Absorbance of 678 cm^{-1} Sulfate Absorption Band Versus Wgt. % of $CaSO_4$ in KBr

$$\frac{\text{weight of KBr disc in reference beam}}{\text{weight of KBr disc containing calcium sulfate}}$$

The weight of the potassium bromide disc in the reference beam was 706.4 mg. The calibration curve for the 1158 cm^{-1} sulfate absorption band is shown in Figure 3. There is still, however, quite a bit of scattering of points.

The calibration plots of Figures 2, 3, and 4 were used to analyze sample No. BCR 1699 which was exposed to flue gas at 1800°F. The amount of sulfate found by the first infrared spectroscopic technique was 26.1% using the calibration plot constructed from the absorbance of the 1158 cm^{-1} sulfate band and 25.4% using the calibration plot of the 678 cm^{-1} sulfate band. The amount of sulfate found by the second infrared spectroscopic technique was 19.9% $CaSO_4$ utilizing the plot of Figure 4. The percent sulfate found in sample No. BCR 1699 expressed as SO_3 as reported by the National Center for Air Pollution Control was 16.5%.

(2) Infrared Quantitative Analysis of Sulfate Utilizing An Internal Standard

Calibration plots obtained using the internal standard method are shown in Figures 5 and 6.

The potassium bromide disc technique employing an internal standard is explained in the following manner. Let the absorbancy of a known material to be assayed at wavelength, λ_k, be given by

$$A_k = \alpha_k \ell_k c_k \tag{5}$$

where α_k, ℓ_k and c_k have been defined by Equation 4 and the absorbance of the internal standard at wavelength, λ_s is given by

$$A_s = \alpha_s \ell_s c_s \tag{6}$$

Now, dividing Equation 5 by Equation 6, we have

$$\frac{A_k}{A_s} = \frac{\alpha_k \ell_k c_k}{\alpha_s \ell_s c_s} . \tag{7}$$

The ℓ's cancel and because α_k and α_s are both constants at the wavelengths at which the measurements are made, and c_s, the concentration of the internal standard is constant, these constants can be accumulated in an overall constant, K, and we have

$$\frac{A_k}{A_s} = K c_k \tag{8}$$

Therefore, a plot of A_k/A_s versus c_k will give a straight line. In this method, it is not necessary to determine α_k and α_s or even to known c_s exactly in order to determine a

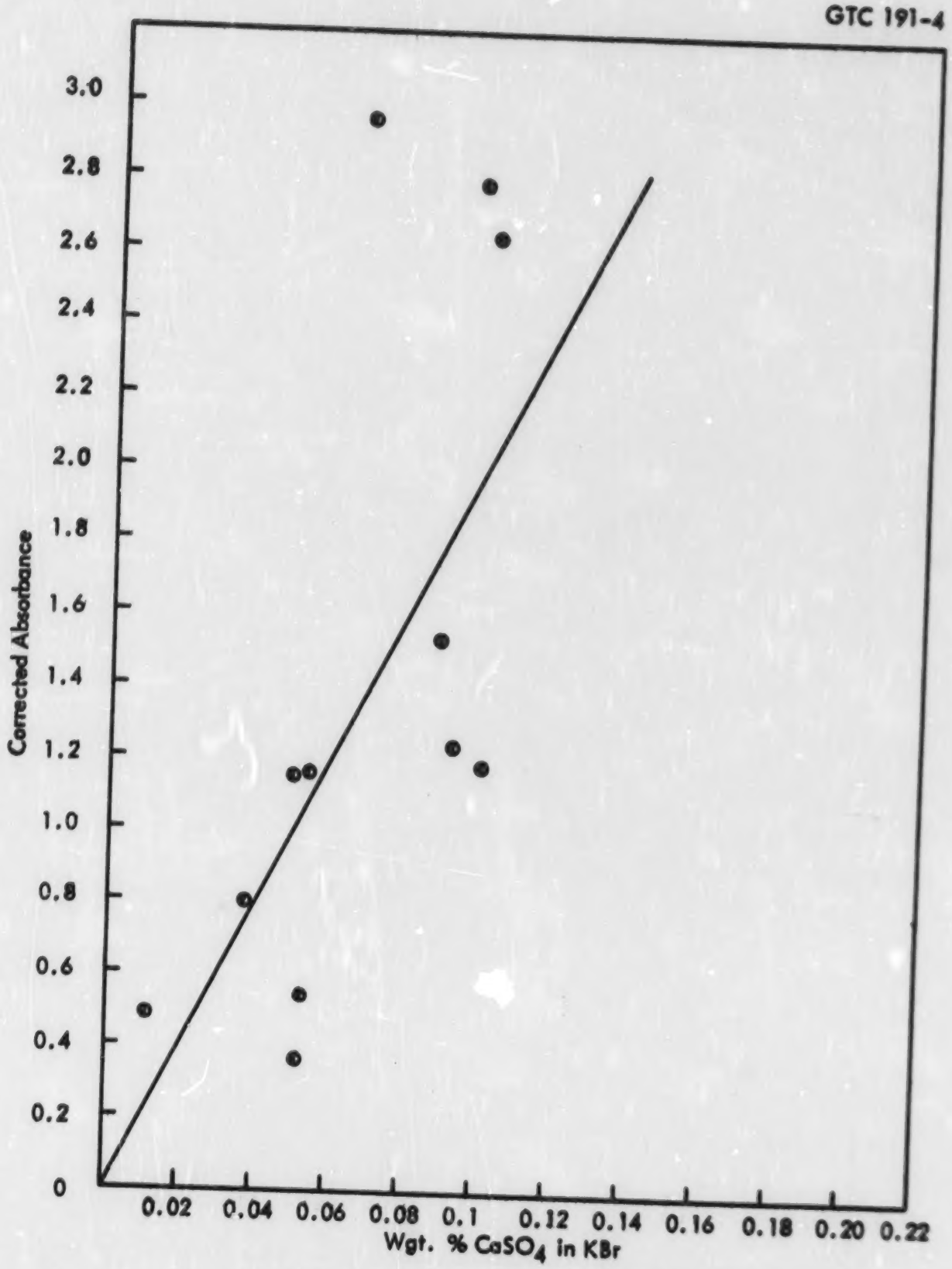


Figure 4. Plot of Corrected Absorbance of 1158 cm^{-1} Sulfate Band Versus Wgt. % $CaSO_4$ in KBr

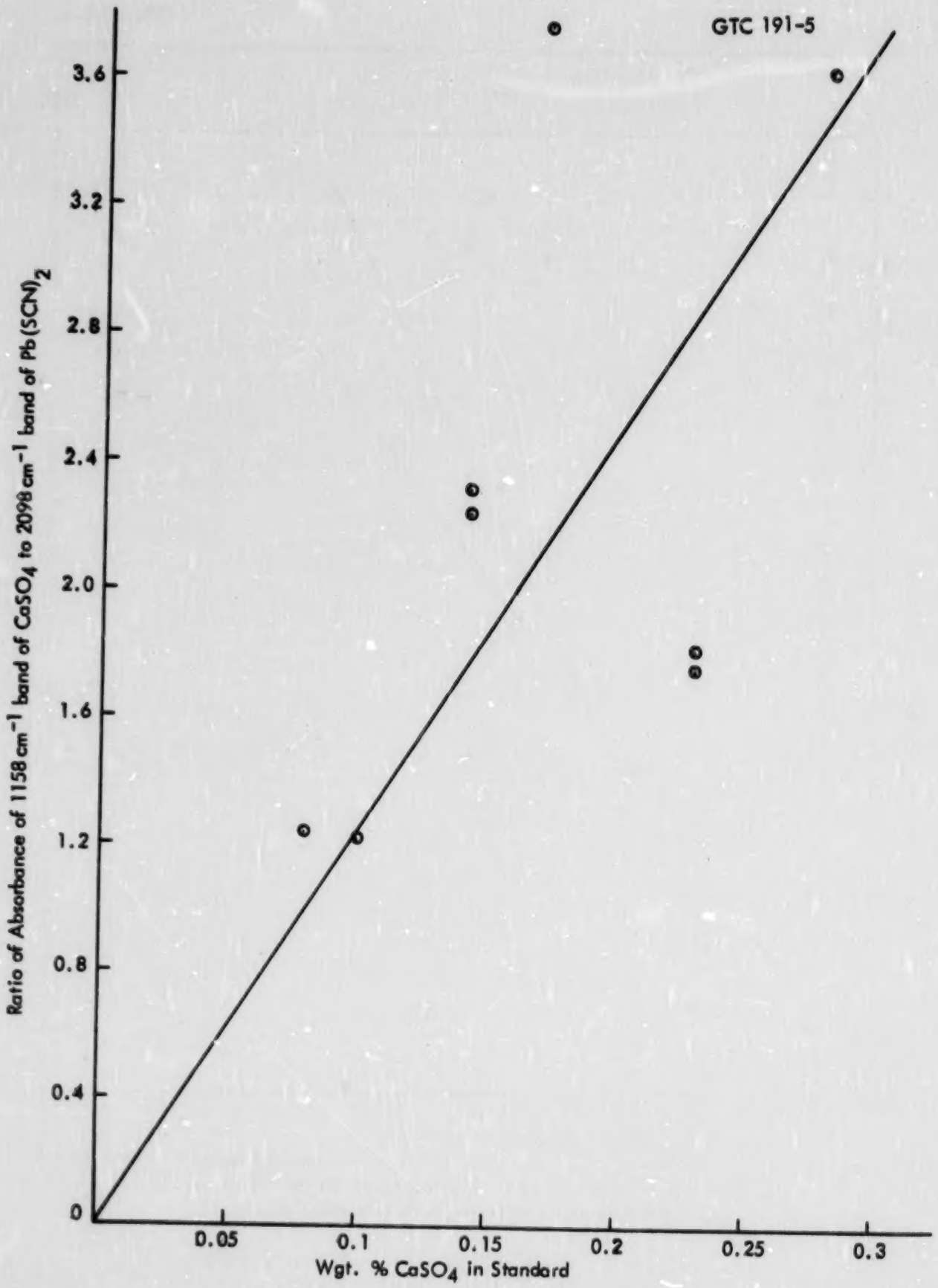


Figure 5. Plot of Ratio of Absorbance of 1158 cm^{-1} band of $CaSO_4$ to 2098 band of $Pb(SCN)_2$ Versus Wgt. % $CaSO_4$ in Standard

GTC 191-6

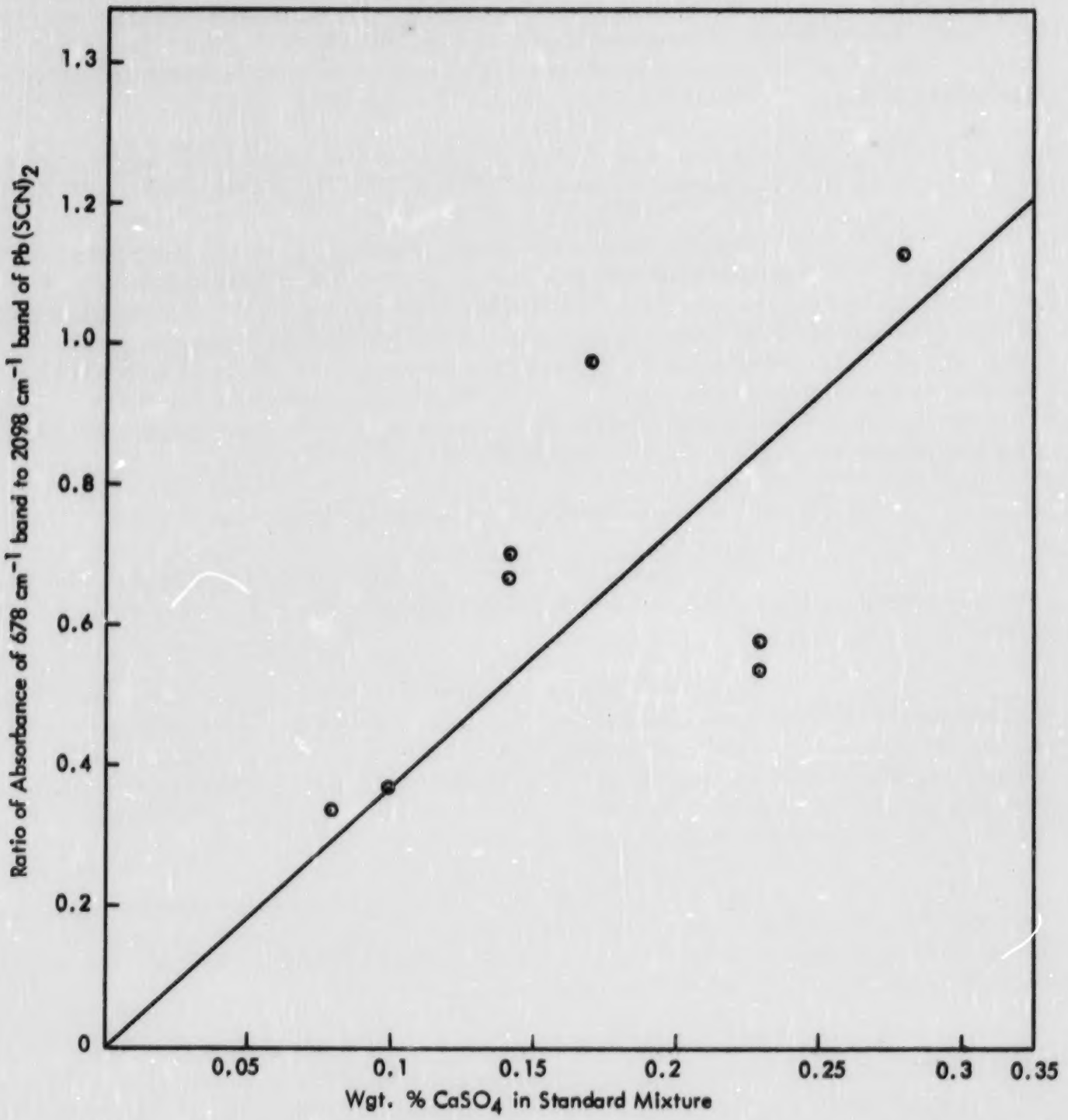


Figure 6. Plot of Ratio of Absorbance of 678 cm^{-1} band to 2098 cm^{-1} band of Pb(SCN)$_2$ Versus Wgt. % CaSO$_4$ in Standard Mixture

working curve. Also, the method eliminates the need to measure the thickness of the potassium bromide disc in the analysis. Calibration data obtained with this method are shown in Figures 5 and 6. Results using this technique to analyze Limestone Sample No. BCR 1699 reacted with flue gas at 1800°F showed a sulfate concentration of 13.4% utilizing the 1158 cm^{-1} sulfate absorption band and 15.5% utilizing the 678 cm^{-1} sulfate absorption band. These values are in only fair agreement with the 16.5% found by wet chemical methods of analysis.

(3) Application of the KBr Technique to the Quantitative Analysis of Carbonate, Hydroxide and Silica

The KBr pellet techniques, without use of an internal standard developed for sulfate were extended to carbonate analysis. The calibration curves for the 1434 cm^{-1} absorption band and the 878 cm^{-1} absorption band are presented in Figures 7 and 8. From the data obtained, the plots indicated a deviation from the Beer-Lambert Law since curved lines are obtained instead of straight line plots. The best free-hand curve has been drawn through the calibration points. The KBr technique was also extended to analysis for hydroxide and silica. Calibration curves were obtained by the same methods used for carbonate. They are shown in Figures 9 and 10.

(4) Use of Freeze Drying and Ion Exchange Techniques

Freeze drying techniques were studied both in conjunction with the use of potassium azide as an internal standard and in combination with ion exchange resins.

The work involving the use of potassium azide was unsuccessful due to interactions and/or reactions between the azide and the HCl used in solution preparations. Indeed, solutions of $CaSO_4$ in dilute HCl, to which were added known amounts of azide, when freeze dried and later converted into pellets, showed calibration data of poor quality. Due to these difficulties, the idea of using azide as an internal standard was not pursued further.

Two forms of the Dowex 50W-X8 sulfonate based ion exchange resin were used in studies aimed at developing an ion exchange technique for dissolution of limestone to be used in conjunction with the KBr pellet technique. Two of the resins forms H^+ and Na^+ were obtained from commercial sources.

With the H^+ form used, problems were encountered in that both reacted with carbonate containing solutions to liberate CO_2. This made this material of little value for use in solubilizing limestone for analytical studies. The Na^+ form of the resin caused another set of unsuspected problems. When distilled water was treated with this material and the resin then removed by filtration, the distilled water was found to contain dissolved species which exhibited, upon infrared examination, bands in the 1450-1400 and 1200-1100 cm^{-1} regions which would interfere with analytical studies. Fortunately, this problem of impurity leaching could be solved by preleaching of all

GTC 191-9

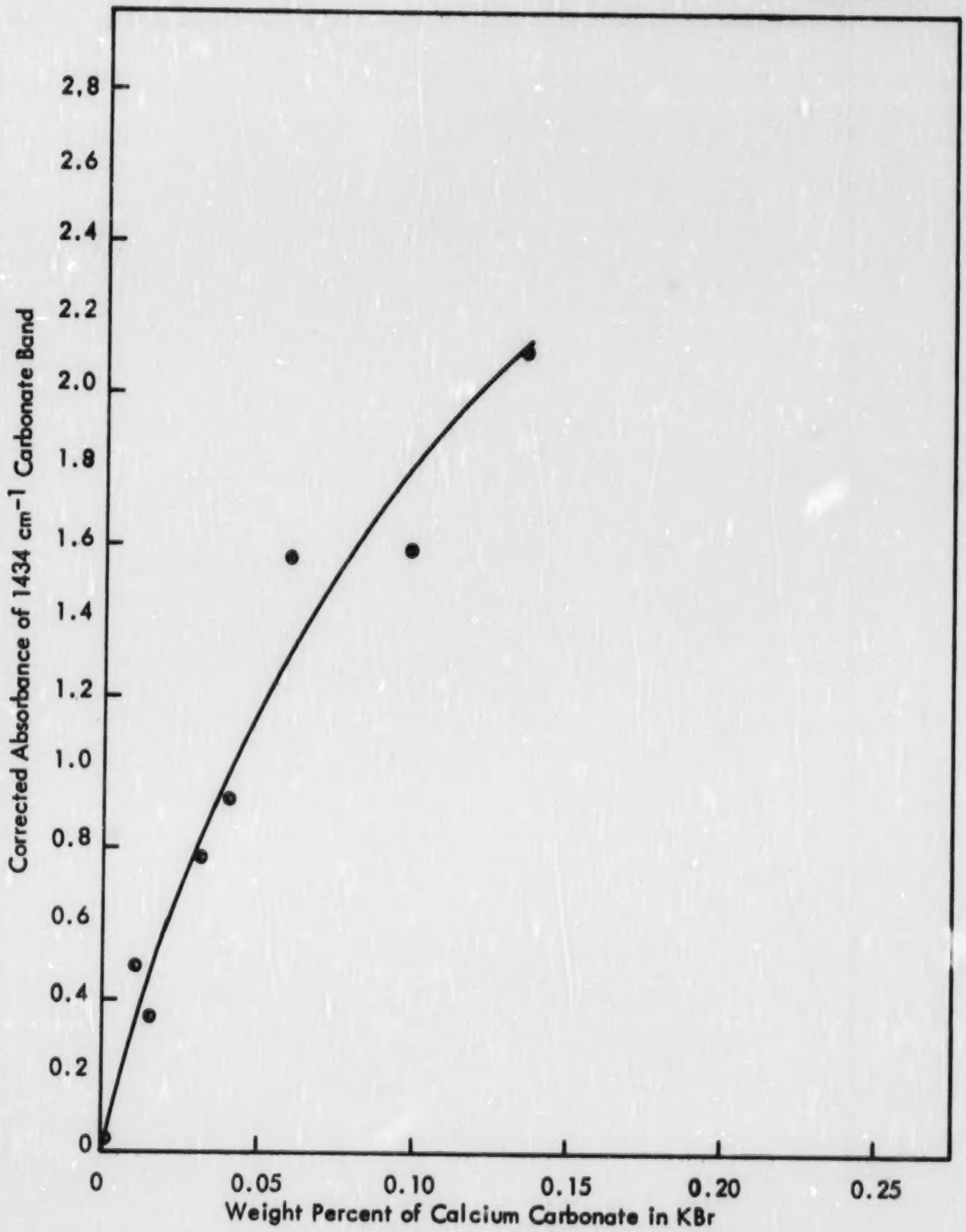


Figure 7. Plot of Corrected Absorbance of 1434 cm^{-1} Carbonate Band Versus Wgt. % $CaCO_3$ in KBr

GTC 191-10

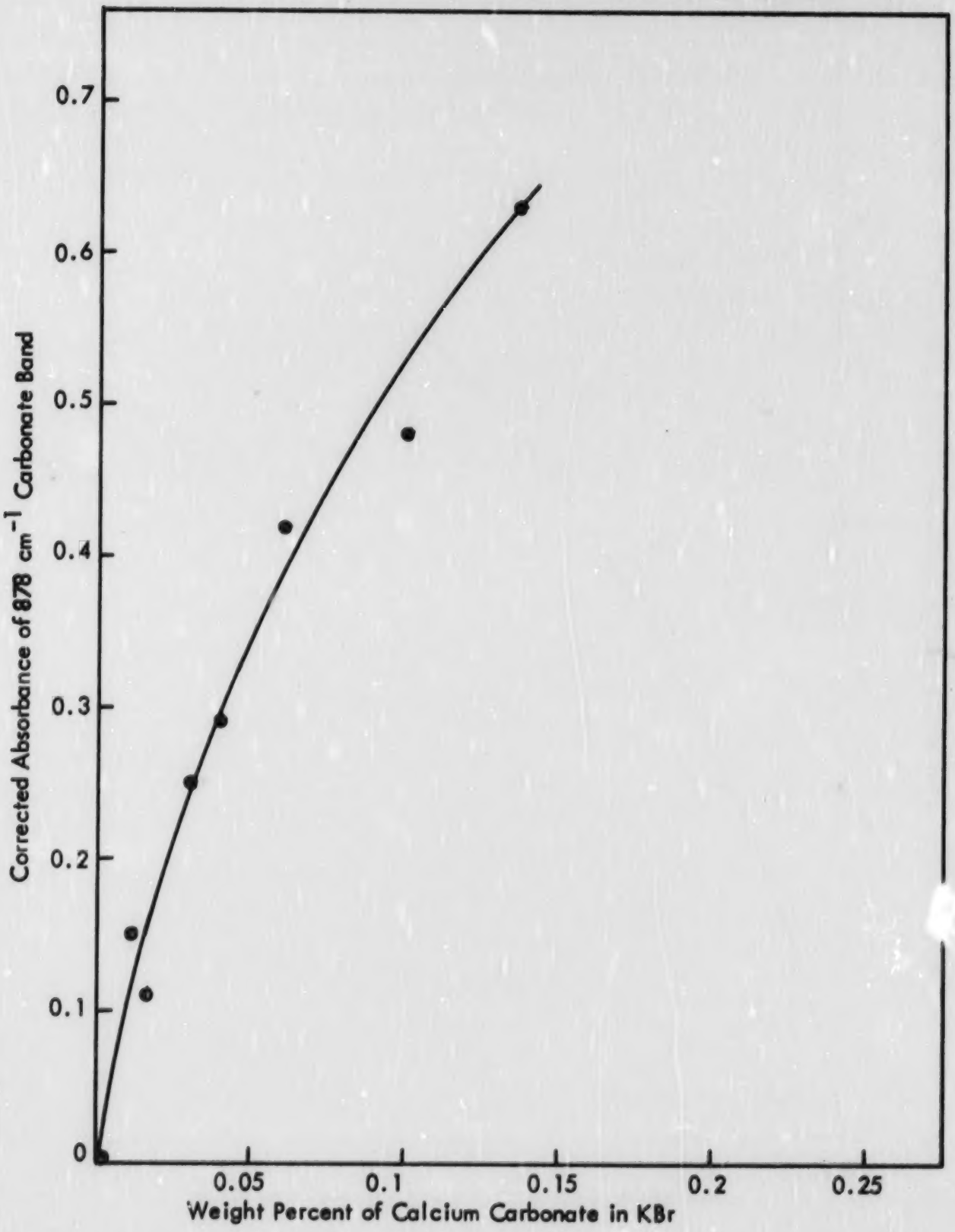


Figure 8. Corrected Absorbance of 878 cm^{-1} Carbonate Band Versus Wgt. % $CaCO_3$ in KBr

GTC 191-11

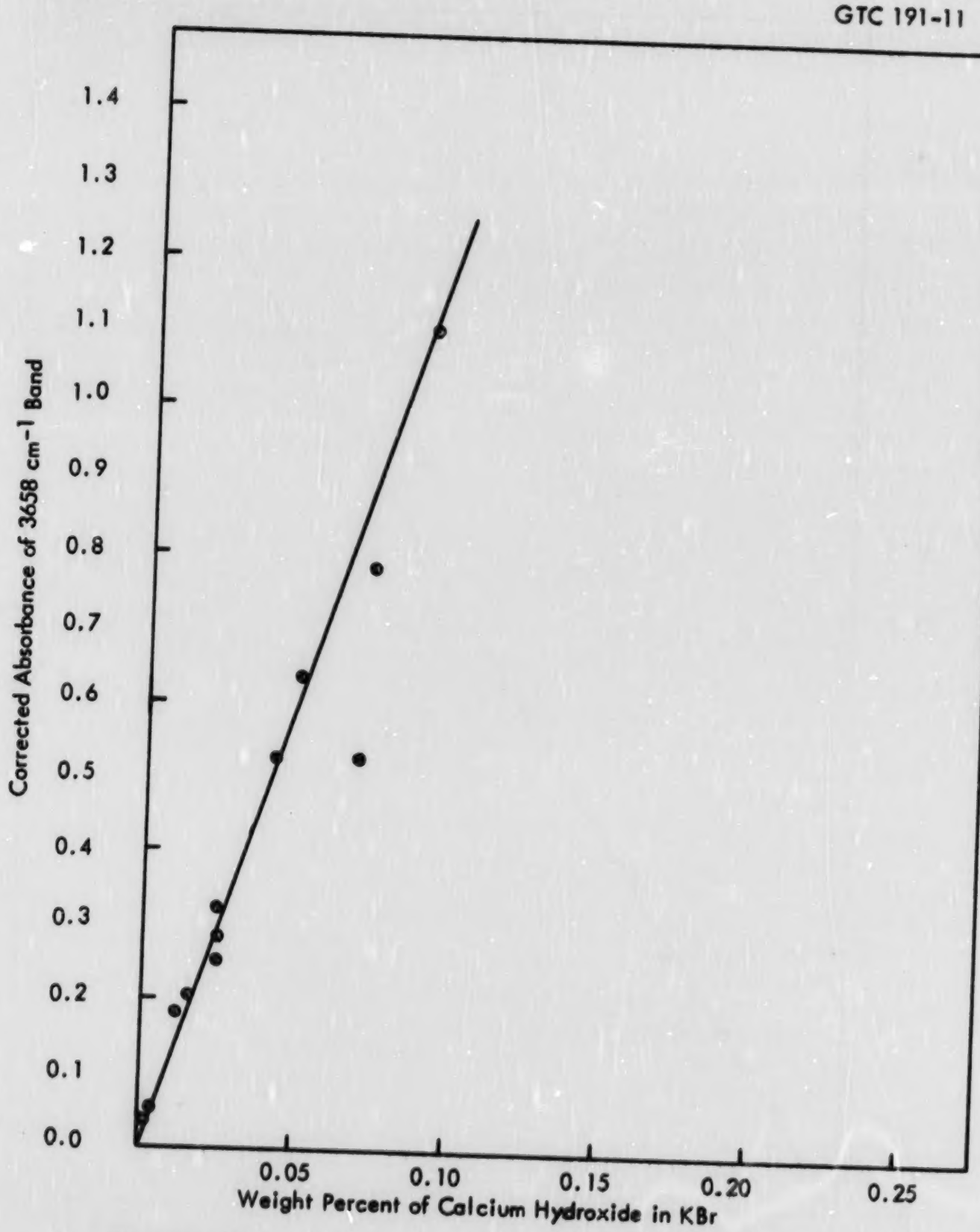


Figure 9. Plot of Corrected Absorbance of 3658 cm^{-1} $Ca(OH)_2$ Band Versus Wgt. % $Ca(OH)_2$ in KBr

GTC 191-12

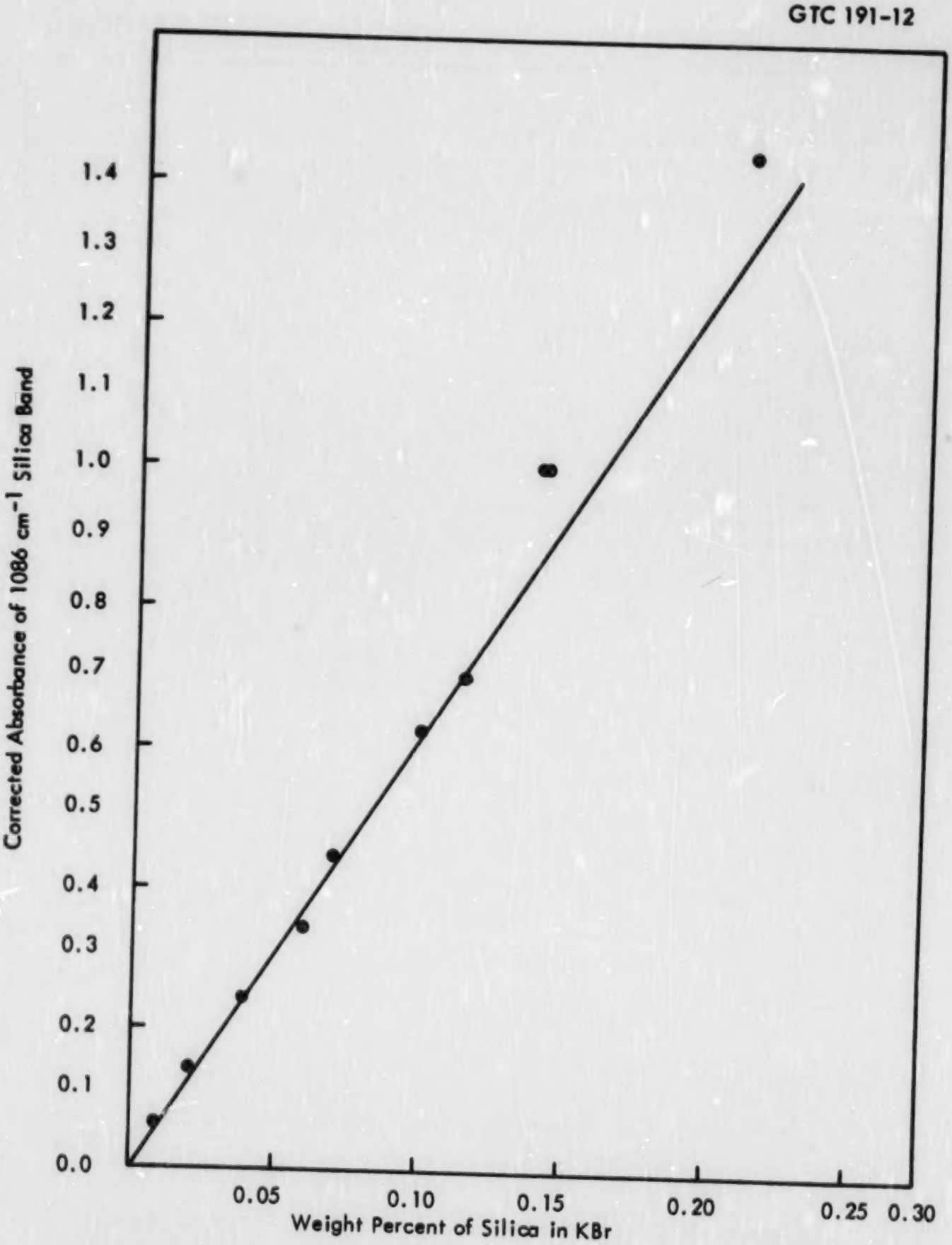


Figure 10. Plot of Corrected Absorbance of 1086 cm^{-1} SiO_2 Absorption Band Versus Wgt. % SiO_2 in KBr

resins used. The Na^+ resins were preleached in warm distilled water for 24 hours twice before use in analytical work. This precedure was found to be satisfactory in that the leached resins were found after this treatment to no longer introduce measurable contaminants into the solutions being treated. It may be noted that the above leaching procedure is similar to that recommended by the manufacturers of a similar material, Amberlite 120, prior to use(5).

Using the leached Na^+ form Dowex resin, calibration curves were made for sulfate and carbonate using the 622 and 1158 cm^{-1} bands for sulfate, and the 1428 and 873 cm^{-1} carbonate absorption peaks. These curves are shown in Figures 11-13.

The general procedure employed in these studies was to prepare solutions of $CaSO_4$ or $CaCO_3$, treat them for 24 hours with the leached ion exchange resin to convert the dissolved salts to their sodium forms, filter out the resin, and then take aliquots of the solutions and mix them with fixed amounts of the KBr standard solution. The resulting solutions were taken and freeze dried, the mixed materials were recovered and pellets were then made and their spectra recorded.

Attempts were made to construct calibration curves for hydroxide using the above techniques, however, spectra of all pellets analyzed revealed that much of the hydroxide had, at some stage, been converted to carbonate. Special precautions, such as prepurging of the $Ca(OH)_2$ solutions with N_2 gas did not eliminate the problem. From studies performed, it was concluded that either the resin reacts with hydroxide to yield carbonate or CO_2 is absorbed from the atmosphere sufficiently readily to make meaningful analysis extremely difficult.

The calibration data obtained above was utilized for analysis of limestone sample No. BCR 1699. 25.8 mg of this material were weighed into a small flask to which was added 10 cc of distilled water and 2.0933 g of doubly leached Na^+ form Dowex resin. The solution was let stand for 16 hours to complete the ion exchange process and the reacted resin was then removed by filtration. The resulting solution was then diluted to 200 cc and two 2 ml aliquots were taken, mixed with a fixed amount of KBr standard solution and the resulting solutions were then freeze dried, the mixed materials recovered, pellets made and spectra run. The spectra revealed no hydroxide to be present in either of the two pellets studies, in agreement with the difficulties found above. Peaks due to sulfate and carbonate were the only ones of sufficient intensity to analyze. Due to the problems related above with conversion of hydroxide to carbonate, analysis was carried out only for the sulfate. The results showed 17.1 and 18.6 percent respectively for sulfate as determined by the 622 cm^{-1} band and 17.8 and 18.8 as determined by the 1158 cm^{-1} band. An analysis of this material previously provided by NAPCA showed 16.5 percent sulfate as determined by a wet chemical technique.

A brief comparison of all results of this sample is now presented.

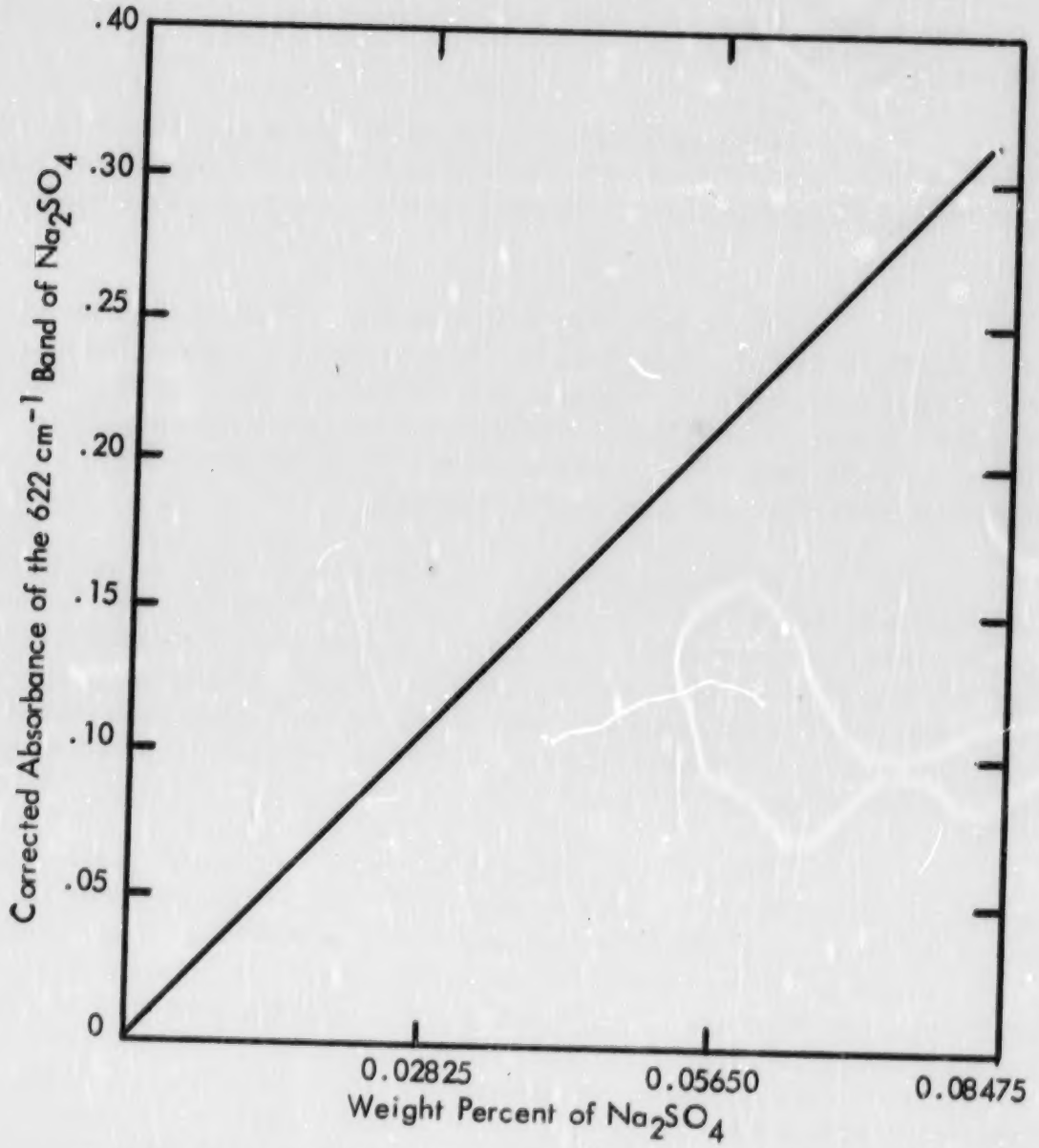


Figure 11. Absorbance vs. Concentration for Sulfate at 622 cm^{-1} from Ion Exchange Method Studies

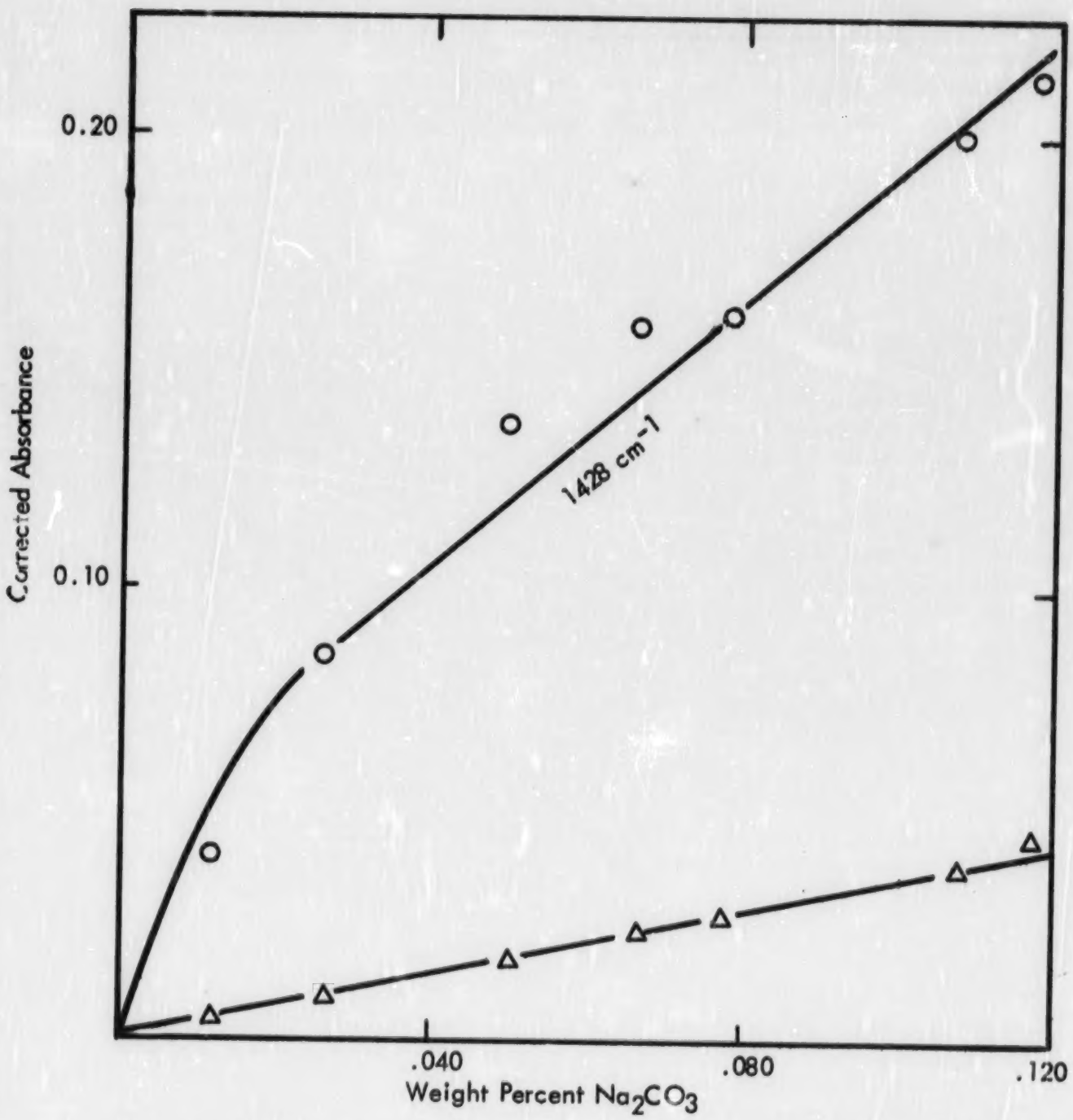


Figure 12. Carbonate Calibration Curves - Ion Exchange Studies

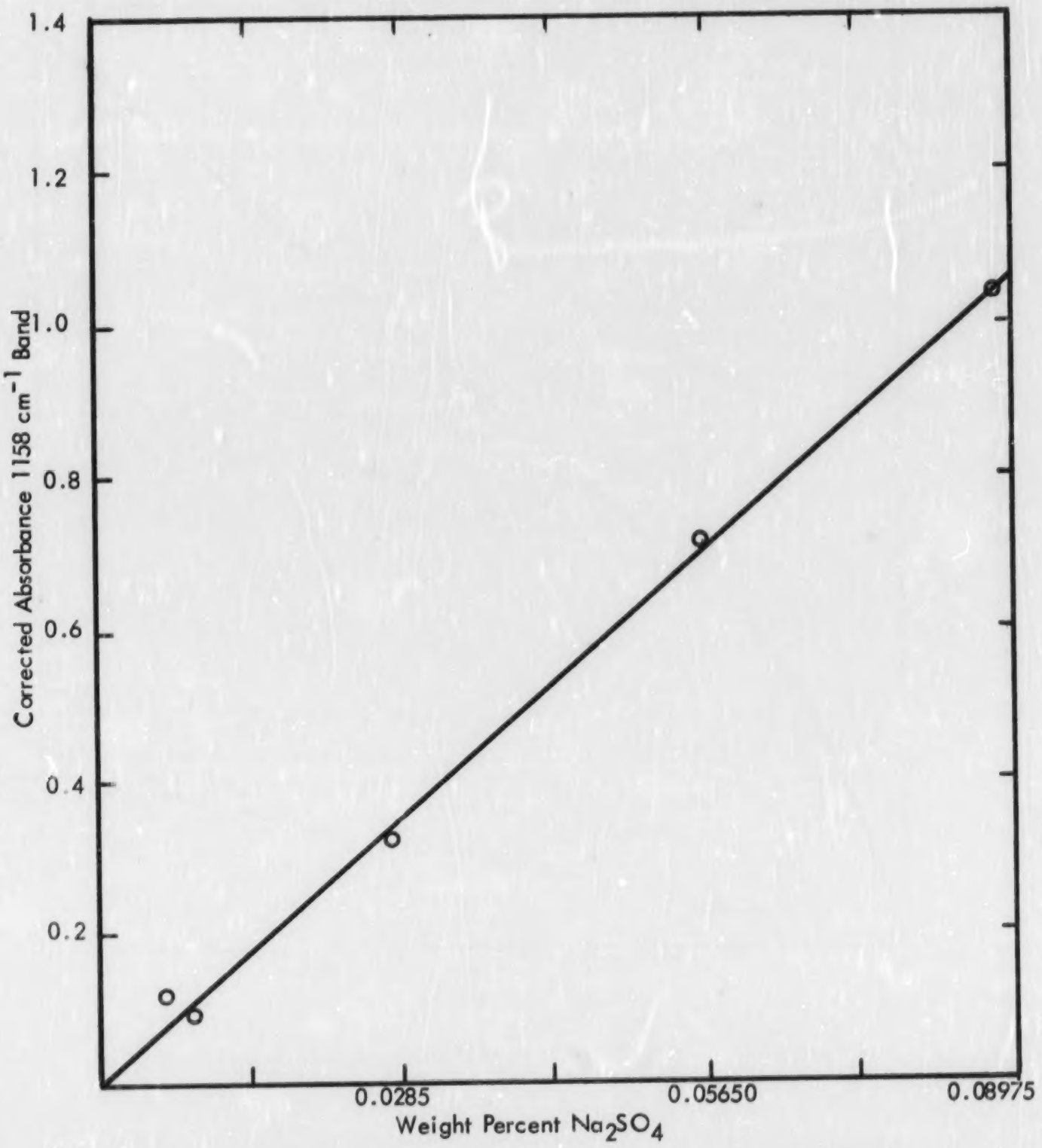


Figure 13. Sulfate Calibration Curve - Ion Exchange Studies

Method	% Sulfate
NAPCA analysis	16.5
Pressed pellet	26.1 - 19.1%
Internal standard method	13.4 - 15.1%
Freeze drying and ion exchange	17.1 - 18.8%, 18.1% average

As can be seen, the freeze drying and ion exchange technique appears to give results of about the same quality as the other techniques previously studied. The average results were about 10 percent different from that obtained by non-spectroscopic methods and the range of results was ±6 percent. However, the difficulties encountered in attempting to analyze for hydroxide and the observed conversion of hydroxide to carbonate seem at present to limit this technique under practical conditions to determination of sulfate and silicate. Under far more rigorous conditions, perhaps the other species may be determinable in a meaningful manner. The range of values (i.e. the data spread) for this method does not seem to be greatly narrowed, although the calibration plots do appear to exhibit far less scatter than those reported for the other pellet techniques. It may be noted that for all of the approaches to development of a pellet method of analysis, either the scatter in calibration data has been too great to yield accurate (± 10%) results, or, as in the case of the ion exchange method, specific difficulties have been encountered in the analysis of one or more species of interest. Also, the necessity of freeze drying of solutions and the time required for use of exchange techniques make the above methods studied of little use in cases where very rapid, accurate analyses for more than one component are desired.

3. Infrared Solvent System

(a) Selection of a Solvent System

One possible method for rapid analysis of reacted limestones is to dissolve these materials in a solvent and determine the constitution of the resulting solutions by infrared quantitative analysis. To properly do this, a satisfactory solvent, which either is infrared inactive or can be made infrared inactive in the regions of interest must exist. Dissolution of limestones, in past work, for wet chemical quantitative analyses has always involved the use of aqueous solutions of various organic or inorganic acids(1). Unfortunately, this approach is of little use in our case as the carbonate content will be converted to CO_2. Another aqueous solvent system, based on the complexing properties with divalent ions of EDTA (ethylenediaminetetraacetic acid) was reported to effectively dissolve limestone without evaluation of CO_2[1]. Unfortunately, water presents problems, due to the high extinction coefficients of its bands, in infrared spectroscopic work.

A series of investigations were therefore aimed at finding either a direct solvent for limestone or a material, to which EDTA could be added with dissolution and then limestone dissolved via complexing with the EDTA. The solubility of $CaSO_4$, $CaCO_3$ and $Ca(OH)_2$ was investigated for each of several materials. In addition, the solubility of EDTA in these solvents was checked. The general procedure used was to attempt to dissolve the EDTA or calcium salt with stirring in the solvent in question. After

a few hours, the solutions were filtered and then freeze dried and the amounts of residues (or dissolvable material) checked. Aside from water, DMSO, and ethylenediamine, both limestone and EDTA were found to be insoluble in all of the liquids studied. For ethylenediamine and DMSO, while solubility of EDTA (ethylenediamine tetraacetic acid) was observed, EDTA saturated solutions failed dissolve any measurable quantities of either calcium sulfate, hydroxide or carbonate. Indeed, while it was possible to prepare at 20 weight percent solution of EDTA in ethylenediamine, this solution failed to show any ability to dissolve the calcium salts. The results of these investigations are shown in Table I. A listing of the materials studied according to polar groups present is given in Table II. As can be seen, materials containing all of the principal polar groups were investigated. Thus, it appears only aqueous EDTA solutions will directly dissolve limestone. In all of the above studies, the acid and disodium forms of EDTA were used in all cases. In the case of ethylenediamine, both materials were observed to possess the same high solubility and inability to complex with calcium salts in this solvent.

An investigation of the solubilities of $CaCO_3$ and $CaSO_4$ in aqueous saturated EDTA solutions was also carried out using the disodium form of EDTA. It was found, however, that the carbonate dissolved in this solution with evolution of CO_2. Accordingly, another saturated solution of disodium EDTA was prepared and to it was added sufficient NaOH to effect complete formation of the tetrasodium form of EDTA. Utilizing this solvent and adding $CaSO_4$ in 50 mg amounts and then stirring to effect more rapid solution, it was found that, at 25°C, 4.55 g of $CaSO_4$ could be easily dissolved in 100 ml of solvent. Similar studies, using calcium carbonate showed a solubility of greater than 3.4 grams per 100 ml of solution.

(b) Design of Cell for Use with Aqueous EDTA

After the solvent system had been chosen, investigations of spectra of sulfate, carbonate, and hydroxide ions in aqueous solutions were undertaken to obtain calibration curves for limestone analysis. Initial investigations showed that water containing cells as thin as .007 mm completely absorbed over most of the infrared region. As .007 mm was the smallest commercially available spacer for use in a liquid cell, it was decided to use an alternative approach. A drop of NaCl saturated water was placed on one of the silver chloride cell windows and the other window then pressed directly to it, without the use of a spacer. (The NaCl solution was used instead of distilled water because this solution was found to spread more easily over the face of the silver chloride window.) This gave a uniform thin liquid film from which the spectra obtained indicated that this technique would result in obtaining useful spectra. Only the region from 3500-3100 cm^{-1} was now completely absorbing. The rest of the spectral region was to some degree useable. Accordingly, an aqueous solution, saturated with both NaCl and sodium sulfate was prepared and utilized in the same fashion. Figure 14a shows the resulting spectrum. The bands at 3300 and 1600 cm^{-1} are due to the water. The 1100 cm^{-1} band is due to sulfate ion. Spectra of only the water film alone (without dissolved Na_2SO_4) were compared with this spectrum and from this an approximate background (Figure 14a) was sketched in. As can be seen, absorbances (uncorrected) of about 0.8 can be achieved for sulfate ion in saturated solutions with this technique. The above techniques were then employed with an

Table I. Solubility of Limestone and EDTA

Solvent	EDTA	Limestone	Solvent+EDTA+Limestone
Acetonitrile	insoluble	insoluble	insoluble
Acetic anhydride	"	reacts to liberate CO_2	reacts to liberate CO_2
Diethylformamide	"	insoluble	insoluble
DMSO	slightly soluble	"	"
Diethanolamine	insoluble	"	"
Acetylacetone	"	"	"
Methanol	"	insoluble*	"
Acetone	"	insoluble	"
Ammonium sulfate	soluble	"	"
Carbon disulfide	insoluble	"	"
CS_2 + diethylformamide	"	"	"
Formamide	"	"	"
Ethylenediamine	very soluble	"	"
Nitromethane	insoluble	"	"
Chloroform	"	"	"
Carbon tetrachloride	"	"	"
Ethylene glycol	"	insoluble*	"
Glycerol	"	"	"
Proplylene carbonate	"	insoluble	"
Butyl acetate	"	"	"
Quinoline	"	"	"
Triethanolamine	"	"	"

*The sodium salts (i.e. Na_2CO_3, Na_2SO_4 and NaOH exhibit some solubility in these solvents.

Table II. Classification of Solvents Used by Polar Groups

Group	Solvents
-OH	water, methanol, diethanolamine, triethanolomine, glycerol, ethylene glycol
$-NH_2$ or $-NR_2$	formamide, dimethylformamide, diethylformamide, diethanolamine, triethanolamine, quinoline, ethylenediamine
$-C \equiv N$	acetonitrile
$-C=O$	acetylacetone, acetone, acetic anhydride
$C=S$	carbon disulfide, dimethylsulfoxide (DMSO)
Esters	proplyene carbonate, butylacetate
Misc.	nitromethane, chloroform, carbon tetrachloride

Na_2CO_3 saturated solution containing a small amount of added Na_2SO_4 (Figure 14b). As can be seen, bands due to both carbonate and sulfate are readily seen, the carbonate absorbing here at ca. 1400 cm^{-1}.

A solution, saturated with the tetrasodium form of EDTA was prepared and saturated with calcium sulfate. The spectrum of a thin film of this solution (Figure 14c) clearly shows a useable sulfate band at ca. 1100 cm^{-1} in addition to a series of bands due to dissolved EDTA. Indeed, from the spectrum present (Figure 14c), sulfate absorbances of as large as 0.8 can be achieved with this simple technique demonstrating the feasibility of this approach.

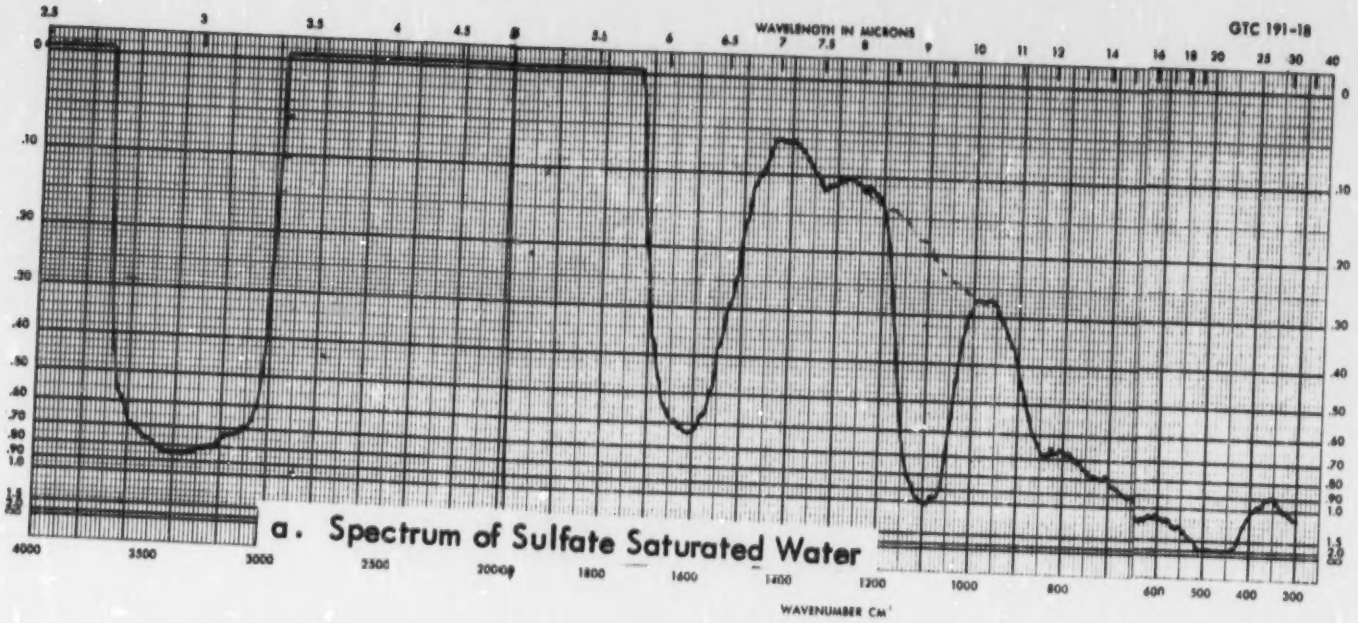
Estimates of the film thicknesses for which meaningful spectra were obtained were made from the volume of one drop of water from the dispensing eyedropper used. From the cell's known width and length, a value of .004 mm was calculated as the maximum film thickness assuming none of the water escaped via flowing over one of the salt plate edges. Probably, however, some solution did escape, although it is fairly certain that at least 50% of that added was utilized as the film. Thus, a thickness of ca. .003 mm appeared to be optimum for our purposes. The problem, however was to obtain this thickness each time. As spacers were not available in such small thicknesses, a special cell had to be designed.

(c) Sulfate Analysis Using the Solvent Technique

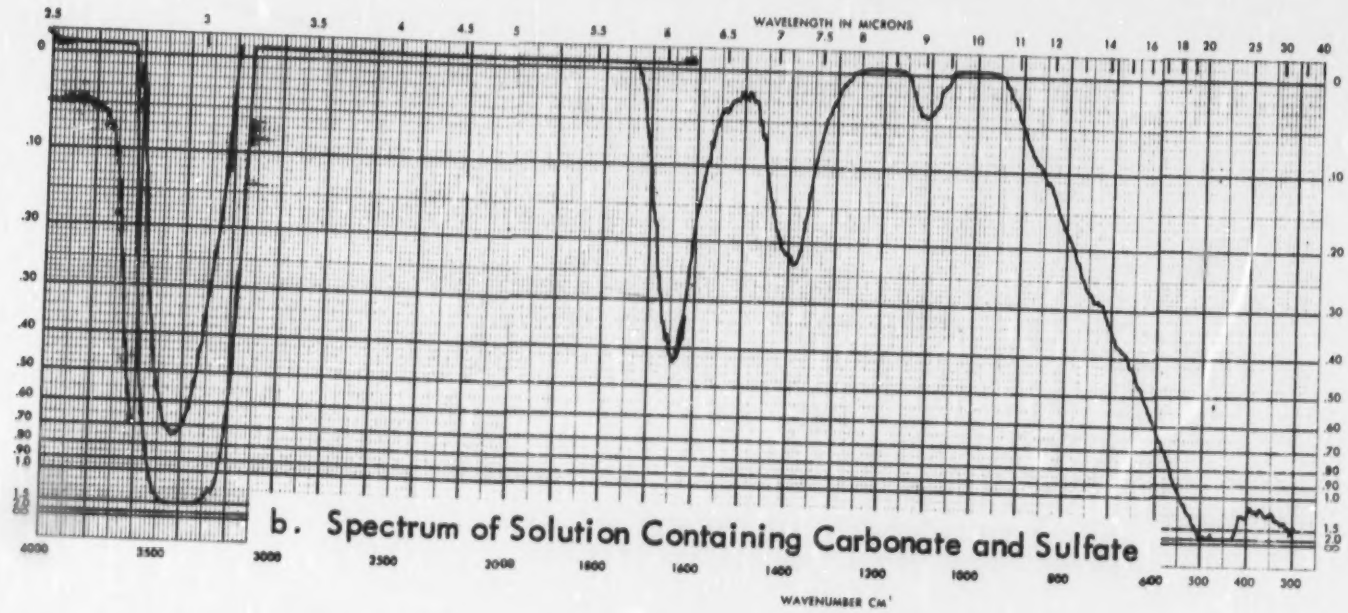
(1) General Procedure

Quantitative determinations for sulfate content of reacted limestones have been conducted by the infrared method using cells such as those shown in Figure 15. The cells consisted of two optically flat silver chloride plates. On the outer portions of the bottom plate was deposited a 0.003 mm thick silver film which served as a cell spacer. The other plate had two small holes drilled through it for admission of sample. This assembly was of the proper size that it could be used in conjunction with commercial cell holders. For this analytical study, a pair of such cells, equal in thickness to within ±2 percent, were used; one containing a saturated aqueous solution of tetrasodium EDTA which was placed in the spectrometer reference beam and the other containing a solution of calcium sulfate or dissolved limestone in this solvent system which was used in the sample beam. All spectra were run on a Beckman IR10 infrared spectrometer.

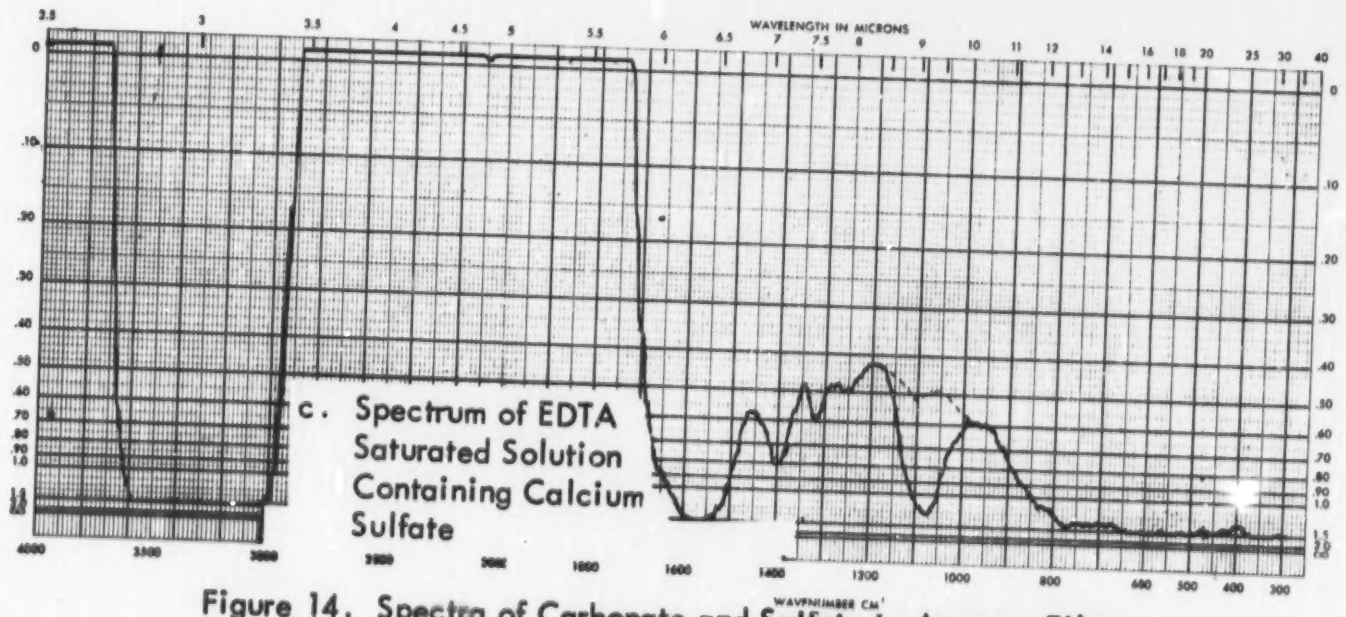
It may be noted that this approach is clearly superior to earlier methods of working with aqueous solutions. Thin film cells used in earlier studies employed thin polymeric films deposited onto the face of a salt plate from solution (i.e. cellulose acetate from acetone solution)[3,6]. This approach was satisfactory for preparing single cells, but is obviously of little use in constructing matched pairs of cells. Past studies by infrared techniques using aqueous solutions were largely limited to qualitative studies[7,10], however, the recent advances mentioned immediately above have made possible some quantitative work, some of which was only recently reported[6].



a. Spectrum of Sulfate Saturated Water



b. Spectrum of Solution Containing Carbonate and Sulfate



c. Spectrum of EDTA Saturated Solution Containing Calcium Sulfate

Figure 14. Spectra of Carbonate and Sulfate in Aqueous Films

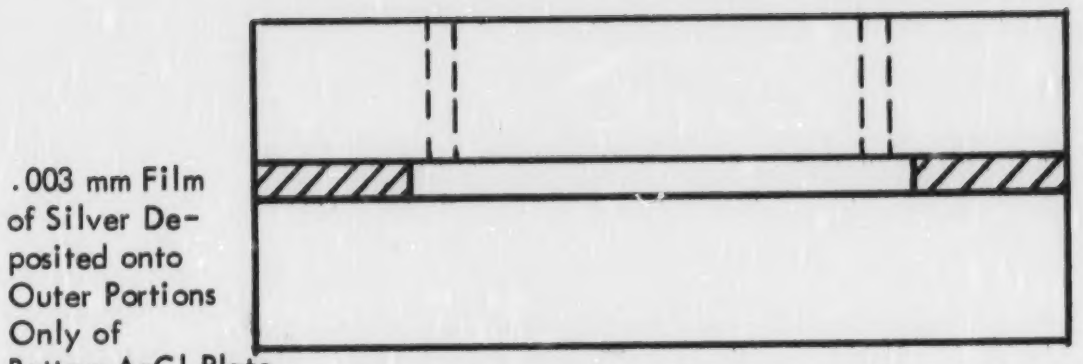


Figure 15. Infrared Cell for Use with Limestone Solvent

The saturated tetrasodium EDTA solutions used were prepared by dissolving this material in distilled water to saturation and storing the resulting solutions over an excess of the EDTA salt. These solutions contained ~290 g/liter EDTA.

Solutions of either calcium sulfate or limestone were prepared by dissolving a known amount of the material of interest in a specified volume of solvent. In the case of some of the limestone samples, difficulties were encountered in dissolving all of the materials. In some cases, an insoluble residue was found to remain. This is in accord with the results of Hill and Goebel[1] who found that limestone constituents such as silica could not be dissolved by EDTA. (These residues were recovered by filtration, washed free of EDTA and incorporated into KBr pellets (2% by weight residue) for analysis.) Spectra of residues obtained in our studies revealed them to contain no sulfate but large amounts of silicates. The results for all of the samples studied are shown in Table III. Calibration curves for sulfate absorbance were obtained from the data on a number of sulfate solutions using the dual cell method described above.

In the data analysis, the absorbances at the sulfate band maximum (1110 cm^{-1}) were measured assuming the background over the sulfate band region was linear. Studies using the dual cells, with only saturated EDTA present in each cell have shown this assumption to be valid. For the calibration studies, a plot was then made of absorbance versus concentration for the $CaSO_4$ samples studied. This is shown in Figure 16. As the same cell thicknesses were employed each time, no corrections had to be made to convert the absorbance data to absorbance per unit thickness.

The analytical results (Table IV), are expressed as percent SO_3. These numbers were arrived at assuming all of the sulfate in the reacted limestone samples was present as $CaSO_4$. Such an assumption agrees well with the findings of Borgwardt(11) in studies of the reactions of calcined limestones with flue gases.

Wet chemical analysis of the limestones studied were conducted by NAPCA to corroborate the infrared results. Specifically, the limestone samples were ground to a fine powder after drying in an oven for one hour to remove physically absorbed water. An accurately weighed sample of 0.2-0.3 g was heated in a mixture of distilled water and cation exchange resin for one hour. The ion-exchange resin(12) serves two purposes in this procedure. The first is that the equilibrium of $CaSO_4$ is shifted toward the right by continually removing calcium ions from the solution and replacing them with hydrogen ions. This releases the sulfate to solution as H_2SO_4. Other slightly soluble sulfates are made soluble in the same manner. Simultaneously the resin renders the solution virtually free of cations which might otherwise interfere with the final titrimetric determination. The solution was filtered through a wad of glass wool into a volumetric flask with washings from the glass wool. A suitable aliquot was taken, made to 80% with isopropyl alcohol and titrated with 0.005 N Ba $(C10_4)_2$ using Thorin indicator(13). As can be seen, good agreement exists for all samples. Duplicate determinations for each of the samples further show that method reproducibility is quite satisfactory.

Some exploratory work was also conducted for analysis of the carbonate and dissolvable silicate contents of limestone using the same techniques. However,

Table III. Spectra of Insoluble Limestone Residues

Sample Number	Band Position (cm^{-1})	Strength	Assignment
187	3650	very weak	OH^-
	1400	very weak	$CO_3^=$
	1240	very weak	?
	1035	strong	Si-O
	970	strong	Si-O
	880	strong	Si-O
	480-570	strong	Si-O
97	1400	very weak	$CO_3^=$
	1025	strong	Si-O
	1250	weak	?
	970	strong	Si-O
	880	strong	Si-O
	490	medium	Si-O
199	1420	very weak	$CO_3^=$
	1250	very weak	?
	1080	strong	Si-O
	1025	strong	Si-O
	935	strong	Si-O
	800	strong	Si-O
	475	strong	Si-O
332	1420	very weak	$CO_3^=$
	1080	weak	Si-O
	1000	weak	Si-O
	880	weak	Si-O
	480	weak	Si-O
330	1440	weak	$CO_3^=$
	1240	very weak	?
	1030	strong	Si-O
	950	weak	Si-O
	880	medium	Si-O
	480	medium	Si-O
377	no residue - sample entirely dissolved		
337	no residue - sample entirely dissolved		

Table III. (cont.) Spectra of Insoluble Limestone Residues

Sample Number	Band Position (cm^{-1})	Strength	Assignment
1351	1410	very weak	$CO_3^=$
	1255	very weak	?
	995	strong	Si-O
	955	weak	Si-O
	900	strong	Si-O
	840	weak	Si-O
	770	weak	?
	500	weak	Si-O
1360	1420	very weak	$CO_3^=$
	1050	strong	Si-O
	940	strong	Si-O
	870	strong	Si-O
	830	weak	Si-O
	765	weak	?
	500	strong	Si-O
1699	no residue - sample entirely dissolved		

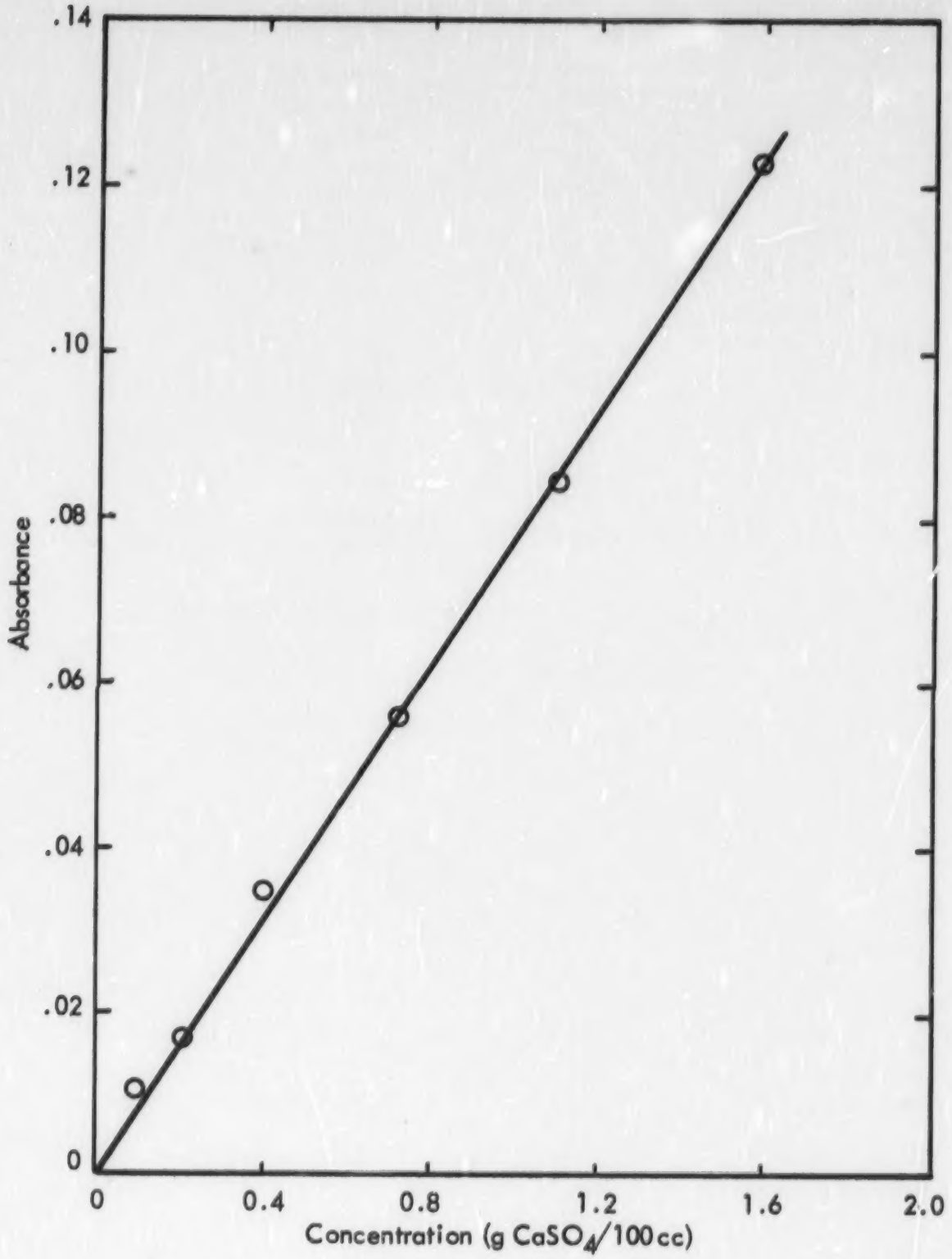


Figure 16. Calibration Curve with .003 mm Cell for Sulfate Ion at 1110 cm^{-1}

Table IV. Analyses of Limestones

Sample Number	Wt % SO_3 By Infrared	Average	Average Wet Chemical Value	Ratio of Infrared to Wet Chemical Values
330	47.26 44.50	45.88	44.5	1.03
199	28.08 27.61	27.84	27.1	1.03
337	47.12 46.29	46.70	42.8	1.09
97	27.88 29.20	28.54	30.4	.95
377	11.56 11.50	11.53	10.5	1.10
187	30.45 29.86	30.15	28.4	1.06
332	18.37 17.61 17.39	17.79	16.5	1.08
BCR 1699 (Solution I*)	17.63 17.40	17.52	16.5	1.06
BCR 1699 (Solution II*)	17.11 18.45	17.78	16.5	1.08
BCR 1351	40.30 41.77	41.03	39.7	1.035
BCR 1360	37.76 40.12	38.94	37.5	1.04

* Solutions I and II of sample BCR 1699 were different concentrations of the same limestone material in saturated tetrasodium EDTA. The second solution, which exhibited the higher pH, was the more concentrated.

the calibration curve obtained for carbonate (Figure 17) exhibited considerable scatter and carbonates were not further examined.

(2) Sulfate Analyses - Results

Calibrations for sulfate were made using solutions of calcium sulfate dissolved in the saturated aqueous tetrasodium EDTA solvent. In these experiments, the test solutions were placed in the cell in the spectrometer sample beam. In the reference beam was placed a duplicate cell containing the saturated EDTA solution, which acted to virtually eliminate most of the spectrum due to water and EDTA. This technique was completely successful for the sulfate calibrations as can be seen in Figure 16, which shows little scatter and good reproducibility using the 1110 cm^{-1} sulfate band.

These techniques were then used to analyze a number of samples of reacted limestone for sulfate content. In all but the two cases of sample 1699, between 1.4 and 1.8 grams of limestone were dissolved in 100 cc of the EDTA solution to gain concentrations in same range as calibration points. For sample 1699, concentrations of ~0.25 and 0.4 g/100 cc were used. Figure 18 shows spectra in the 1750-800 cm^{-1} region of both dissolved limestone and of the EDTA solvent above using a single thin film cell. As can be seen, differences due to the limestone exists at ~1440 cnd 1110 cm^{-1}. Spectra obtained using a set of cells as described above, show essentially only these bands. Table IV shows the analysis results along with results obtained by the National Air Pollution Control Administration's (NAPCA) Cincinnati laboratories for these same samples using wet chemical analysis methods. As can be seen, the values obtained by the infrared method are somewhat high. A discussion of the reasons for this is given below:

(3) EDTA-pH Studies

The pH's of the solutions of limestones and of the pure saturated tetrasodium EDTA aqueous solution were determined with Grammercy Universal Indicator using the color charts provided by the manufacturer. Over the pH range 8.5-10.0, this indicator changes slowly from green to blue to violet to reddish violet. The exact procedure employed in these investigations for each solution was to add 1 mil of the solution in question to 5 mil of distilled water and then add a few drops of indicator, shake the solution to insure proper mixing and observe the resulting color. The results for each of the solutions used are given in Table V.

A graph of the data given in Table V appears in Figure 19. As can be seen, there is a direct correlation between deviation in pH, from that of the pure EDTA solution and percent error in the analytical results. Thus, solutions which had pH's lower than that of the reference solution gave consistently low analysis results, while solutions of increased alkalinity gave consistently high values.

The above findings can be readily interpreted by examination of the spectra of the various forms of EDTA. The spectrum of the disodium salt (Figure 20) shows a sharp band at ca. 1180 cm^{-1}. Single cell spectra of the tetrasodium form of EDTA, both in the presence andabsence of limestone are shown in Figure 18. Comparison of the two

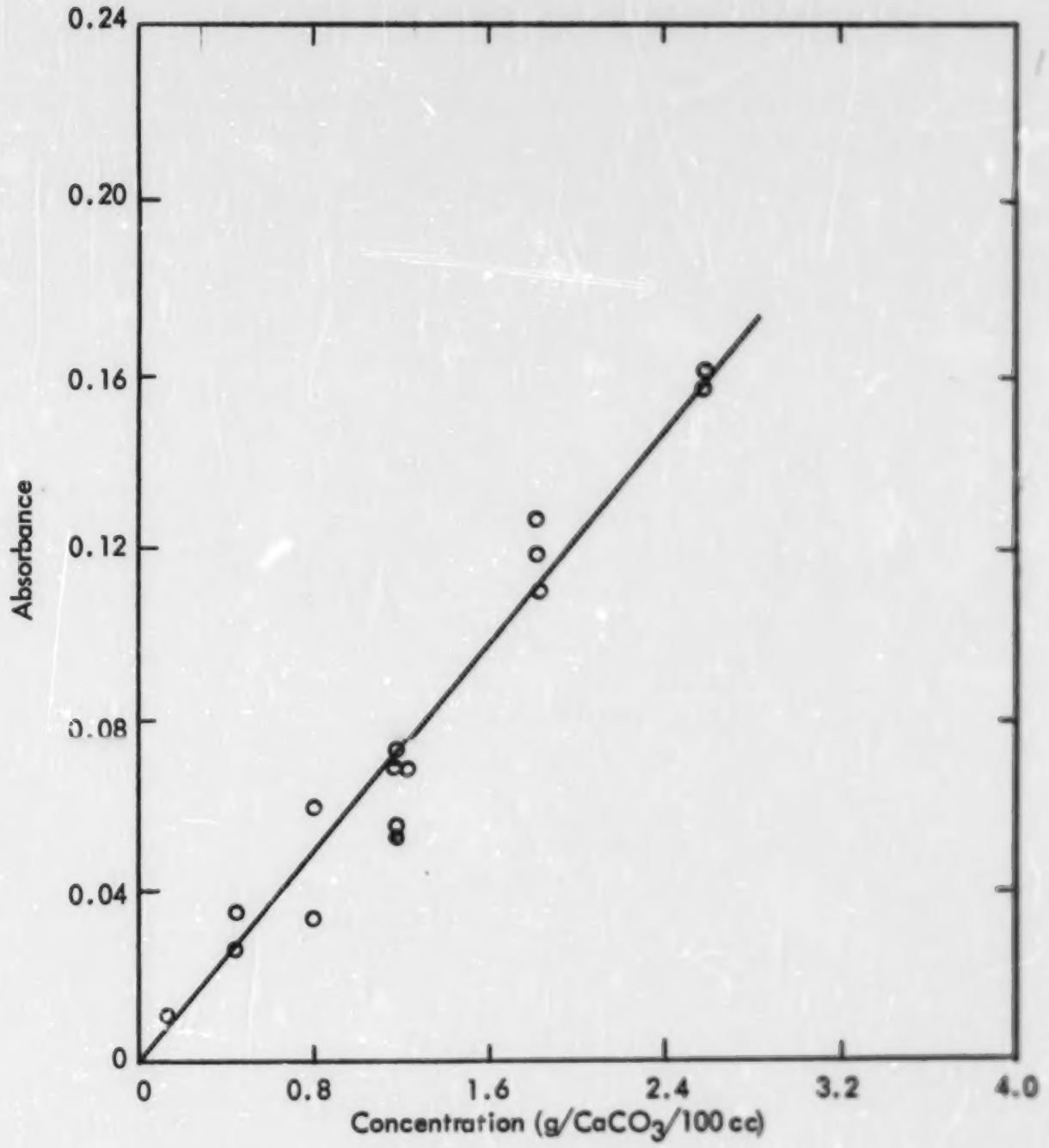


Figure 17. Calibration Curve with .003 mm Cell for Carbonate Ion at 1400 cm^{-1}

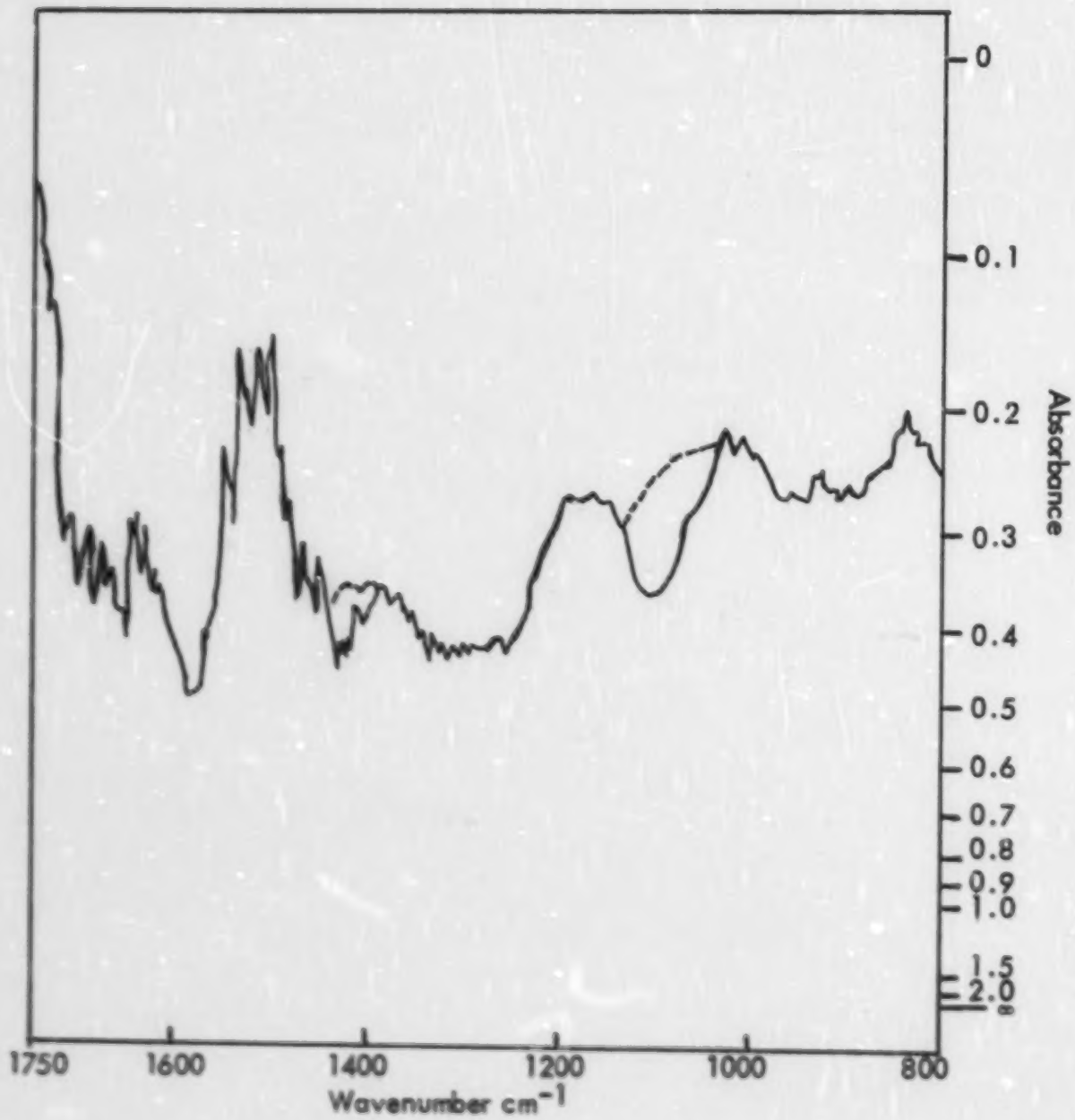


Figure 18. Spectra of EDTA Solution Alone and EDTA Solution Containing Dissolved Reacted Limestone

Table V. Effects of Solution pH on Analysis Errors

Solution Sample Number	pH	% Error In Analysis
EDTA	9.0	-
330	9.0	3% high
199	9.0	3% high
187	9.2	6% high
97	8.8	5% low
337	9.3	9% high
377	9.5	10% high
332	9.6	8% high
1351	9.3	6% high
1360	9.4	8% high
1699 (#1)	9.3	3.5% high
1699 (#2)	9.5	4% high

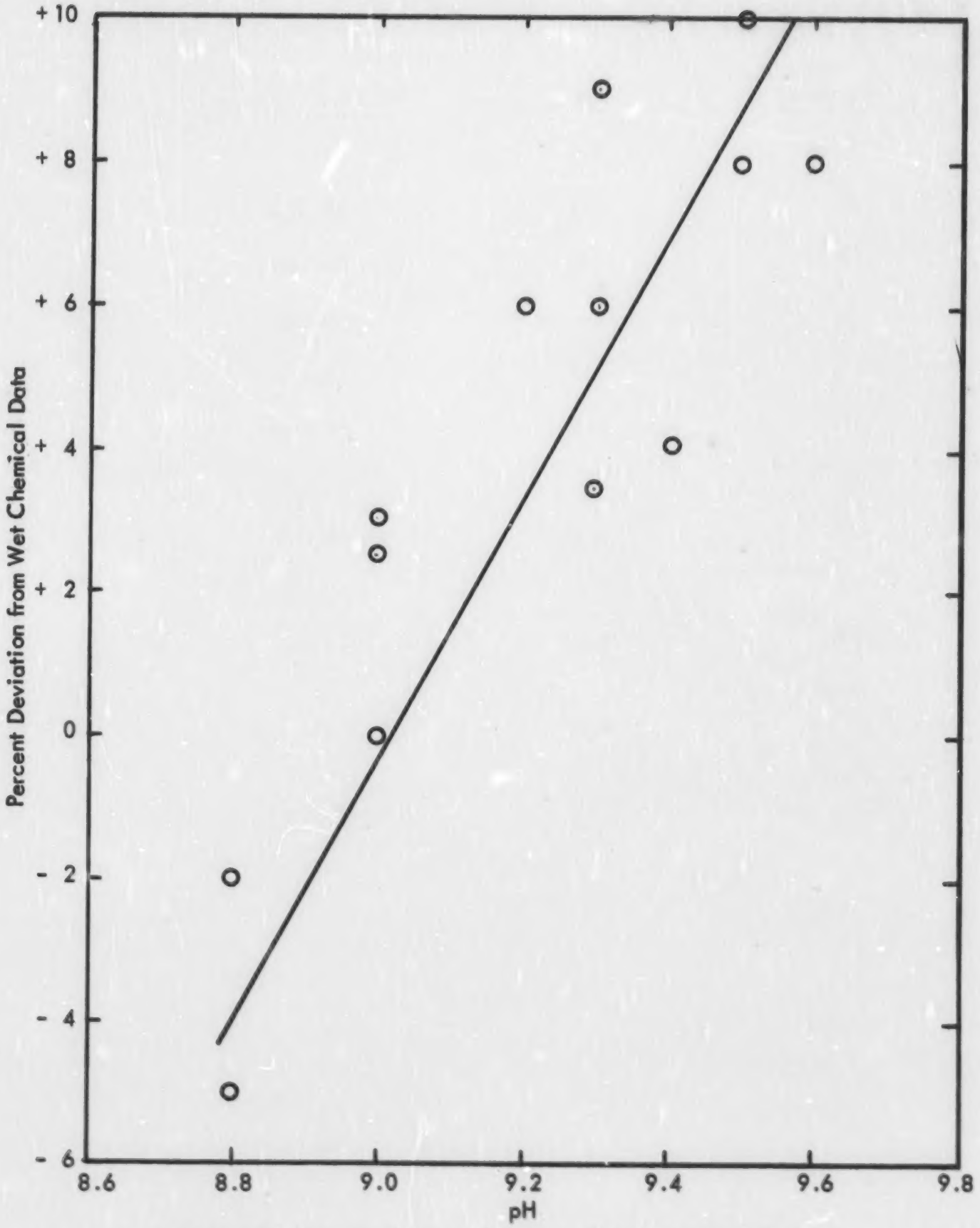


Figure 19. Percent Error vs. Solution pH for Limestone Analyses

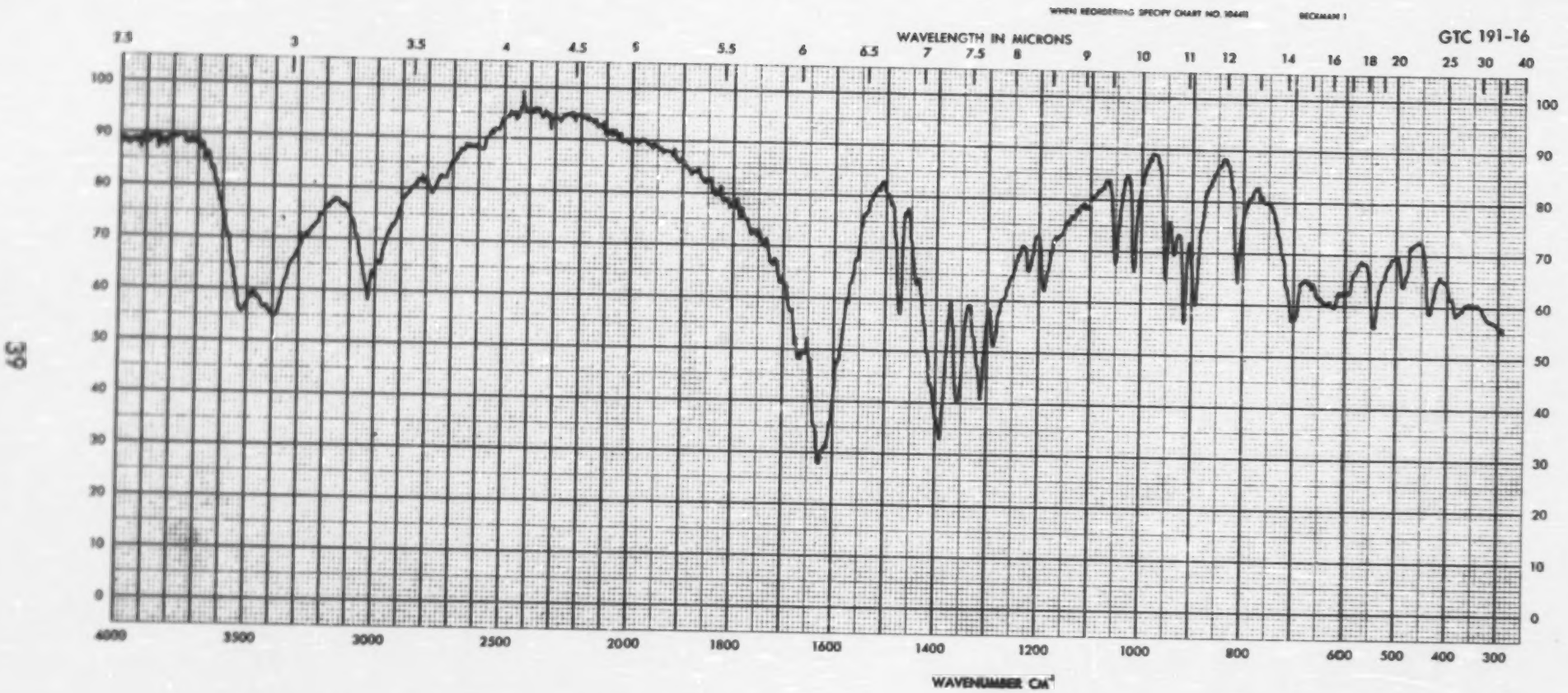
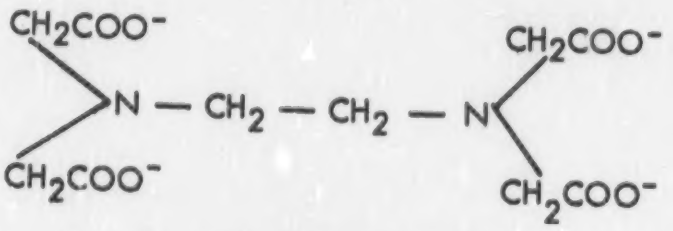


Figure 20. Infrared Spectrum of the Disodium Salt of Ethylenediaminetetraacetic Acid (KBr Pellet)

spectra shows this band has shifted to ca. 1135 cm^{-1} and broadened. The ph's in solution of the two materials are 4.8 and 9.0 for saturated solutions of the two EDTA forms. By making the tetrasodium EDTA solutions more alkaline, perhaps, further shifts in he 1135 cm^{-1} band could occur for the following reasons:

a). The carbon nitrogen stretches for — C — NH_2 groups occur in the region 1200-1000 cm^{-1}, the exact position depending on other groups banded to the carbon and on the degree of protonation of the NH_2 group in the medium in which it is being examined.

b). For EDTA salts, the structure is:



c). The protonation equilibrium

$$-NR_2 + H_2O \rightleftharpoons NR_2H + OH^-$$

is pH dependent. Indeed, making the solution more alkaline should shift the equilibrium to the left and thus bring the C—N absorption band closer to the 1110 cm^{-1} region being examined.

Figure 21 shows a plot of the change in solution pH on limestone dissolution versus % SO_3 (or sulfate content) of the sample. The line drawn is that to best fit the data. As can be seen, the samples containing the least sulfate (and hence the largest amount of unreacted oxide and hydroxide) clearly cause the greatest changes in pH toward alkalinity.

Figure 22 shows a plot of percent SO_3 variation* between duplicate runs on the same samples as a function of the order in which the samples were run. As can be seen, with increasing cell use (rising run number), the data spreads on individual samples rises. This can be attributed to factors such as cell erosion and general wear and/or oxidation of the silver spacers and silver chloride windows. With the cell arrangement, it is impossible to repolish one of the windows due to the silver film present. Window repolishing would necessitate evaporation of a new spacer film making such an approach unrealistic. For future work, an improved cell should either have more wear

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*By percent SO_3 is meant the difference between two duplicate runs on the same sample. This, for example, if answers of 18 and 20 percent were found, the percent SO_3 variation plotted would be 20-18 or 2.0.

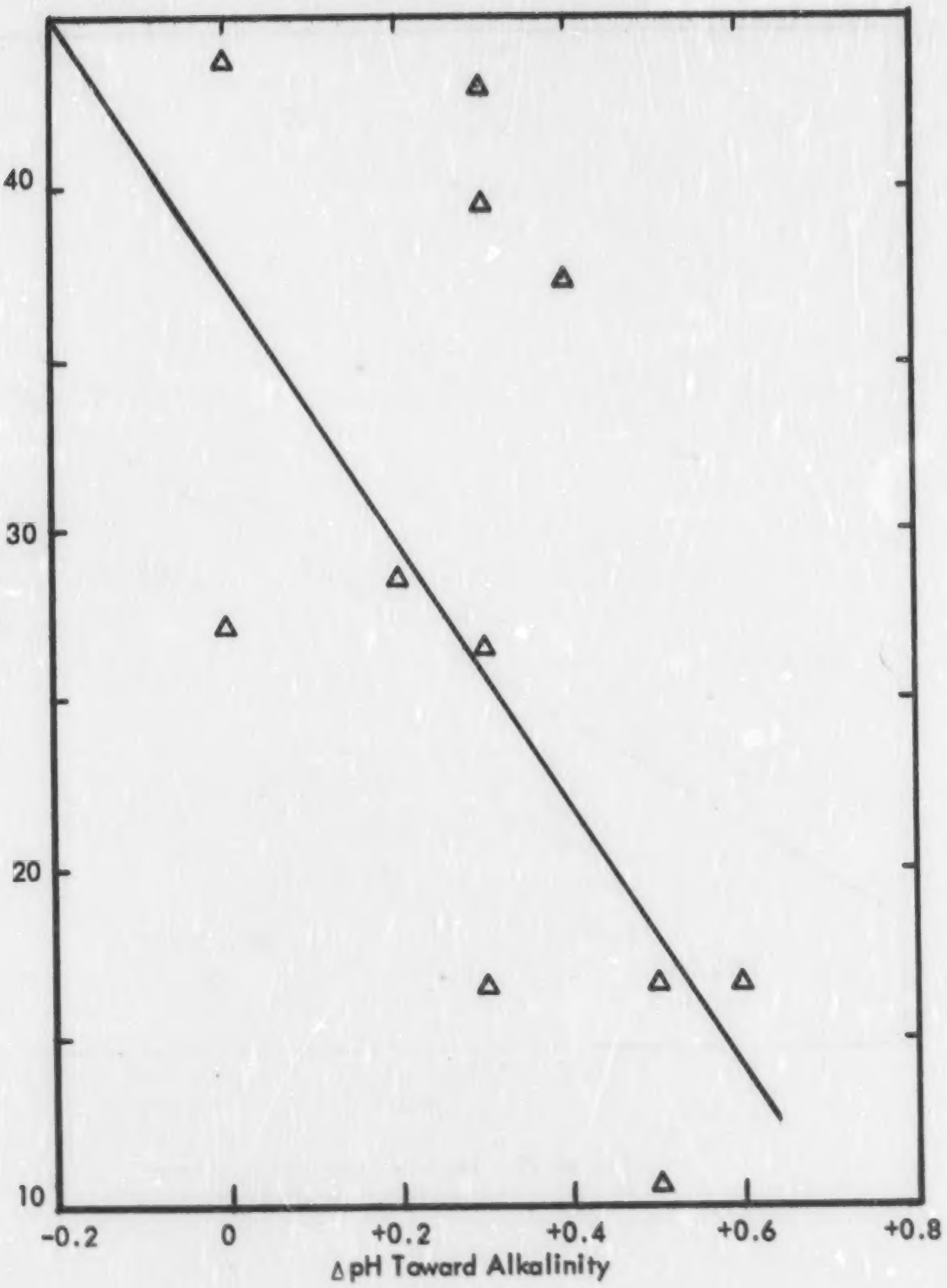

Figure 21. Effect of Sample Sulfate Content on Solution pH Change

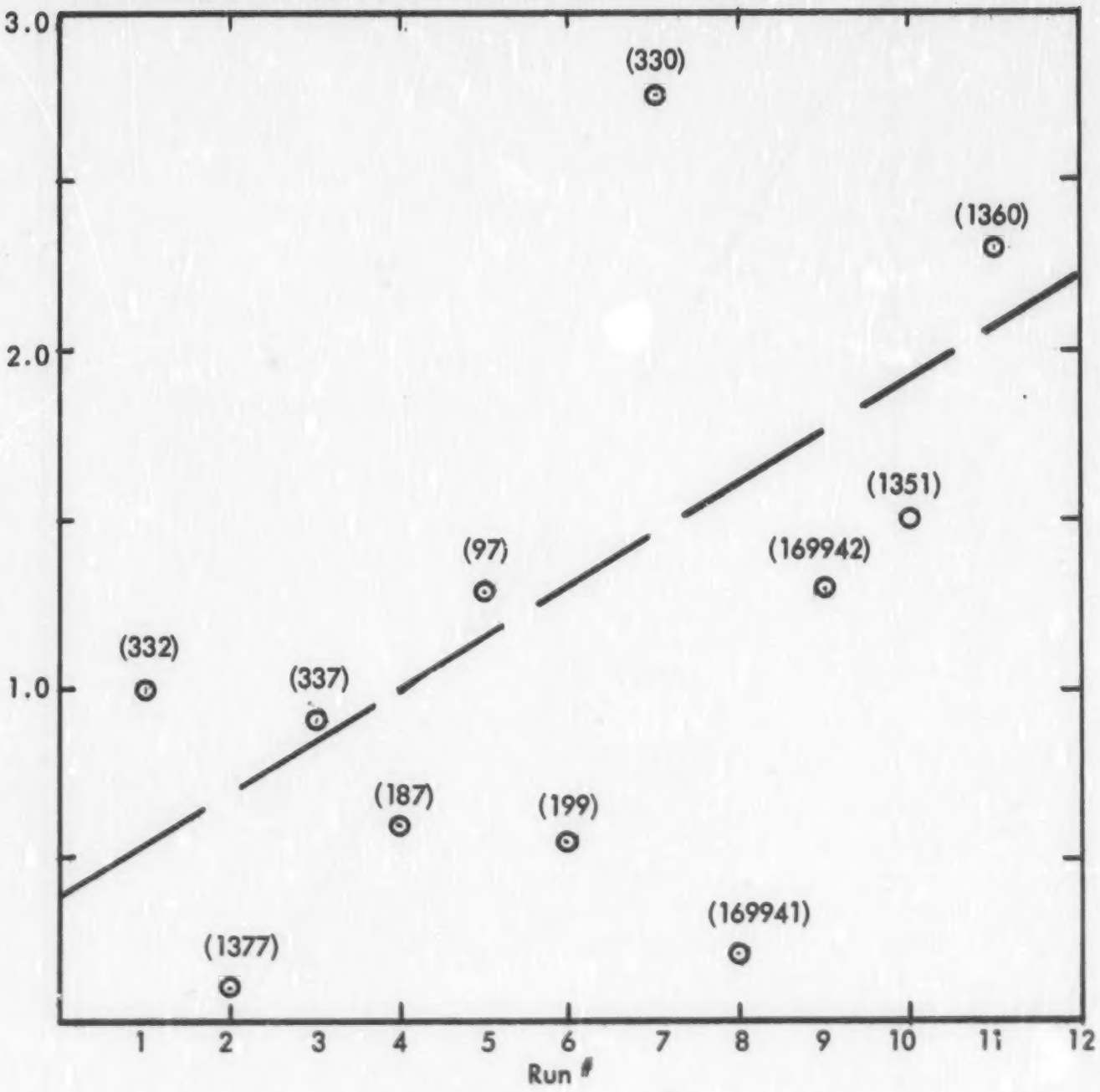

Figure 22. Percent SO_3 Variation as a Function of Cell Age

resistant materials than silver or AgCl or use a demountable 3 micron spacer so windows can readily be repolished.

(d) Analysis for Other Limestone Constituents

Using the same methods as for sulfate analysis, a calibration curve, as shown earlier was constructed for carbonate using the 1400 cm^{-1} $CO_3^=$ band. Unfortunately, the data showed considerable scatter, particularly at lower concentrations of carbonate. From spectra obtained for the dissolved EDTA, it was ascertained that the cause of this was small differences in cell thicknesses. EDTA displays a number of intense bands in the 1400 cm^{-1} region, but not near 1110 cm^{-1}. Thus, analysis for carbonate can only be conducted, at present using such a procedure, with very concentrated solutions.

Spectra run by the techniques above of sodium silicate dissolved in the saturated EDTA solutions revealed bands of useable intensity at ca. 1100, 1020 and 850 cm^{-1}. Thus, dissolved silicates can also be determined by the above techniques.

Spectra run of pure D_2O revealed absorption only in the 2600-2000 cm^{-1} and 1250-1150 cm^{-1} regions. Addition of either LiOH, NaOH, or KOH to D_2O yield bands at ca. 3400 cm^{-1} and 1650 cm^{-1} as is expected for OH groups tied to similar species by hydrogen bonding, as is the case in the liquid phase(14). In a series of experiments the percentage of NaOH in D_2O was increased over a series of runs. The 3400 and 1650 cm^{-1} bands were both observed to increase with increasing hydroxide concentrations. These experiments, using D_2O as solvent, were performed using a single .003 mm cell with a wire screen in the reference beam. In another series of studies, spectra were run of solutions of $Ca(OH)_2$ in EDTA saturated D_2O. In these experiments, a thin (.003 mm) cell filled with EDTA saturated D_2O was used in the reference beam. Spectra obtained revealed strong broad bands at 3400 and 1650 cm^{-1}.

Using one of the thin film cells, spectra were also recorded of solutions of $LiNO_3$, $NaNO_2$, Na_2HPO_4 and Na_2SO_3 to demonstrate that other ions, such as nitrate and phosphate could also be quantitatively determined in solution by the infrared method. For these studies, no cell or screen was used in the reference beam. The spectra for the above salts were obtained in both H_2O and D_2O. In both solvents, the following band positions were noted:

NO_3^-	1370 cm^{-1} (S)	830 cm^{-1} (W)
NO_2^-	1240 cm^{-1} (S)	1350 cm^{-1} (W sh)
$HPO_4^=$	1075 cm^{-1} (S)	985 cm^{-1} (M)
$SO_3^=$	920 cm^{-1} (S)	

(e) Scale Expansion Technique Studies

Using the scale expansion accessory and an external chart recorder, efforts were made in this period to determine the minimum amount of dissolved carbonate, in the absence of EDTA, which would be detectable with the thin film cell method. For these studies, a duplicate cell, filled with water, was used in the reference beam. All

of these spectra were run at low scanning speed and fairly low gain to minimize noise problems, and the 10X scale expansion setting was used. The results are given below:

Na_2CO_3 Solution Concentration	10X Expanded Absorbance	Unexpanded Absorbance	Unexpanded Noise Level
0.10 g/100 cc	0.05	0.005	0.0003
0.01 g/100 cc	0.007	0.0007	0.0003
0.001 g/100 cc	not detectable	—	0.0003

As can be seen, the minimum detectable amount of dissolved carbonate observable with our apparatus appears to be about 10^{-2} g/100 cc. From other calibration data, a calculated value for the minimum observable concentration can be calculated assuming an inherent noise level of ± 0.0003 absorbance. Here, the minimum useful absorbance observable would be ~0.0006, twice the inherent noise level. From the slope of the carbonate calibration curve reported earlier, an absorbance of 6×10^{-4} would correspond to a carbonate concentration of ca. 9×10^{-3} g/100 cc, in good agreement with the experimental value reported above.

As the extinction coefficient for sulfate, as judged by the calibration curves obtained earlier, is of the same order of magnitude as that for carbonate, the minimal detectable concentration of sulfate should also be ca. 10^{-2} g/100 cc.

(f) Discussion of Results with Thin Film Cells

The methods developed in this study using very thin cells appear to give satisfactory results for sulfate analysis and probably could also be directly utilized for silicate and hydroxide determinations. The problem of carbonate analysis, however, remains to be solved. At the present state of development, our techniques would require application of additional methods, such as are due to Robinson(15), to sort out contributions of EDTA absorption to the scatter in the carbonate studies. For the other species, however fortunately, such an elaborate procedure should not prove to be necessary.

The studies using D_2O have revealed this to be a superior solvent for analytical purposes to water. Also, it may be possible in D_2O based solvents to separately determine the hydroxide and unreacted oxides of limestone. Thus, if one were to use Na_2D_2 EDTA and Na_2H_2 EDTA in D_2O as solvents, for CaO and $Ca(OH)_2$, the reaction occurring would be:

1. Na_2D EDTA + CaO $\longrightarrow$ D_2O + $CaNa_2$ EDTA
2. Na_2D_2 EDTA + $Ca(OH)_2$ $\longrightarrow$ 2 DOH + $CaNa_2$ EDTA
3. Na_2H_2 EDTA + CaO $\longrightarrow$ H_2O + $CaNa_2$ EDTA
4. H_2O + D_2O (excess) $\longrightarrow$ 2 DOH
5. Na_2H_2 EDTA + $Ca(OH)_2$ $\longrightarrow$ H_2O + $CaNa_2$ EDTA

From the above reactions, one can see that using the deuterated EDTAin D_2O one would measure only the hydroxide present, while using the dihydrogen EDTA, one

could determine oxide plus hydroxide. Thus, from the two measurements one could obtain the concentrations of oxide and hydroxide present in reacted limestones.

To extend the techniques developed for sulfate analysis further will require construction of improved cells. As can be seen from Figure 22, the silver chloride cells possess ugly problems which tend to limit their usefulness. More resistant materials, clearly, should be used. In future studies, materials such as ZnS or ZnSe could be employed and a better spacer material, such as Teflon or tantalum could likewise be utilized to improve cell lifetimes. Also, better ways of filling of the cells should be developed. The standard filling arrangement for commercial cell holders works well if the sample cavity to be filled is sufficiently thick; however, for our cases to fill the cells and have them free from air is a tedious procedure.

A summary, from all the data presented above, it can be seen that a rapid accurate, infrared method for sulfate analysis has been developed and that this general method should also be applicable to other uses of interest. All that will have to be done to achieve this will be to obtain the necessary calibration curves under controlled pH conditions.

B. DEADBURNING AND MgO HYDRATION STUDIES

1. Introduction

The dry limestone injection process for sulfur dioxide removal from flue gases offers a number of advantages based on its low cost and simplicity of operations. However, in certain cases a number of problems have been formod which are related to incomplete reaction of the limestone. One of the possible causes of this incomplete reaction is the phenomenon called deadburning, wherein the calcined limestone becomes relatively inactive toward either hydration or chemical reaction due to either collection of impurities at its surface or to a large loss of surface area and pososity.

A number of studies have been made of the deadburning phenomenon; however, much disagreement still exists as to the importance of several of the variables involved. Thus, while some authors have related reactivity to pore volumes and surface areas available for reaction(16-18), others have stressed the possible influence of various solid state reactions which can occur with impurities during calcination. Impurities during calcination. Impurities such as SiO_2, Al_2O_3, Fe_2O_3, phosphates, sulfates and potassium and sodium salts are known to differ widely with sources(19), and it is known that above 1750°C reactions between CaO and SiO_2 do occur which result in formation of surface silicates. Indeed, it has been found that limes high in silica may react with water like hard burned (i.e. low surface area) materials even though extensive sintering did not occur(20).

An extensive study of the pyrochemical reactions occurring in impure limestone has been conducted by Lee(21). With increasing calcination temperature several reactions occur including formation of silicates, ferrites and alumina ferrites, all of which lead to inert materials which, at high temperature, melt and diffuse readily to the surface causing particle shrinkage and reduction in porosity. On cooling, it has been found that these

materials, particularly the ferrites, recrystallize on the surface providing a barrier against reaction[21]. Thus, it is conceivable that part of the deadburning problem can perhaps be traced to formation of layers of inert materials over portion of surfaces. This paper presents a study using infrared spectroscopic methods which attempts to assess some of the reactions with impurities which occur during the calcination process.

2. Experimental

The three series of limestone samples used in this study were supplied by the National Air Pollution Control Administration, Cincinnati, Ohio. These samples were calcined at the specified temperatures in a rotary kiln under an inert atmosphere for two hours. Table VI shows the chemical compositions of each of these samples. Additional limestone samples used to study the hydration of MgO were also supplied by NAPCA. For these, calcinations were carried out at 1800°F in a rotary kiln and slaked in distilled water. The reacted samples were exposed to 2800 ppm SO_2 at 750°F.

Spectra were run on the various samples using the KBr pellet technique. Specifically, the limestone powders were mixed mechanically in a Wig-L-Bug with KBr powder for 30 seconds and the resulting mixtures were then pressed into pellets and spectra runs. Each pellet contained ca. 0.1% by weight of limestone material. For the studies using pure MgO and CaO, the same mixing and pellet preparation techniques were used. All spectra were recorded with a Beckman IR 10 Spectrophotometer using the double beam mode and slow scan speed.

3. Results and Discussion

(a) Calcination Temperature Studies

The three series of samples obtained from NAPCA were used for studies of the effect of calcination temperature on the positions and intensities of the Si-O stretching bands. As can be seen from Table VI, two of the materials were high calcium limestones and the third was a dolomitic material. Spectra run on all these samples showed only bands due to hydroxide, carbonate and silicate present. The hydroxide bands were probably due to reaction of the calcined limestones with water vapor in the air during specimen preparations. No bands attributable to ferrites or aluminates could be seen. All three sets of materials contained ca. 2% silica by weight.

Table VII shows the spectra obtained for the three series of limestones as a function of calcination temperature. Assignments could made for all bands except a weak one at ca. 1260 cm^{-1}, which occurred for all samples. Careful examination of the data in Table VII reveals that for all three materials:

(1) the bands above 1200 cm^{-1} in frequency do not change appreciably in position with increasing calcination temperature.

Table VI. Compositions of the Series of Limestones Used in Deadburning Studies

Sample Series	Percent by Weight of Constituent (as supplied by NAPCA)								
	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	TiO_2	Na_2O	K_2O	MnO_2
100	1.40	<0.2	0.27	1.77	95.0	0.03	<0.02	<0.1	<0.03
101	2.25	<0.2	0.31	2.42	94.0	0.03	<0.02	<0.1	<0.03
102	2.63	0.72	0.70	36.0	58.0	0.05	0.06	0.47	<0.03

Table VII. Spectra of Limestones as a Function of Calcination Temperature

101 Series

1700°F	2000°F	2300°F	2600°F	3200°F	Assignment
3655 s	3655 s	3655 s	3650 s	3650 s	OH^-
2960 w	2955 vw	2960 w	2960 w	2960 w	$CO_3^=$
2350 w	2340 w	2350 w	2350 w	2350 w	$CO_3^=$
1800 w	-	-	-	-	$CO_3^=$
1440 s	1440 s	1440 s	1440 s	1440 s	$CO_3^=$
1260 w	1250 w	1235 w	1235 w	1230 w	?
1120 w	1110 w	1110 w	1100 w	1095 w	Si-O
980 s	995 m	995 w	1000 w	1005 w	Si-O
915 w	920 w	940 w	940 w	950 w	Si-O
875 w	875 w	875 w	875 w	875 w	$CO_3^=$
850 w	850 w	850 w	855 m	860 m	Si-O

102 Series

3650 s	3650 s	3650 s	3650 s	3650 s	OH^-
2920 w	2930 w	2930 w	2930 w	2930 w	$CO_3^=$
2350 w	2350 w	2350 w	2350 w	2350 w	$CO_3^=$
1440 s	1440 s	1440 s	1440 s	1440 s	$CO_3^=$
1260 w	1260 w	1260 w	1260 w	1260 w	?
1115 s	1115 s	1105 m	1105 w	-	Si-O
993 s	995 s	1005 mb	1010 wb	1010 wb	Si-O
890 s	910 w	920 vw	920 vw	920 vw	Si-O
875 w	875 w	875 vw	875 vw	875 vw	$CO_3^=$
845 w	845 w	845 m	855 m	865 m	Si-O

100 Series

3650 s	3650 s	3650 s	3650 s	3650 s	OH^-
2940 w	2940 w	2940 w	2940 w	2940 w	$CO_3^=$
2350 w	2350 w	2350 w	2350 w	2350 w	$CO_3^=$
1440 s	1440 s	1440 s	1440 s	1440 s	$CO_3^=$
1260 w	1260 w	1260 w	1260 w	1260 w	?
1120 vw	1110 vw	1110 vw	1110 vw	1105 vw	Si-O
1000 s	1005 m	1010 w	1010 vw	1010 vw	Si-O
910 w	925 w	925 w	925 w	925 w	Si-O
875 w	875 vw	875 vw	-	-	$CO_3^=$
845 vw	860 vw	855 w	865 w	870 m	Si-O

s = strong
w = weak
vw = very weak
b = broad
m = medium

(2) the 1115 cm^{-1} band decreases in intensity per unit weight of sample with increasing calcination temperature and shifts to lower frequencies.

(3) the 990 cm^{-1} band shifts to ca. 1010 cm^{-1} with increasing calcination temperature and decreases strongly in intensity.

(4) the 890 cm^{-1} band shifts to ca. 920 cm^{-1} and decreases in intensity with increasing calcination temperature.

(5) the 845 cm^{-1} band shifts to 865 cm^{-1} and increases in intensity with rising calcination temperature.

(6) Generally, the four above bands broaden considerably with increasing calcination temperature.

Figure 23 shows a plot of the fraction of total shift observed as a function of calcination temperatures for the averages of the three bands of principal interest (i.e. 995, 890 and 845 cm^{-1}). Here, the average band positions and shifts for each temperature for all samples were calculated and the average band shift is plotted against calcination temperature. As can be seen, the band at ca. 930 and 1010 cm^{-1} seem to exhibit the same dependence on calcination temperature, while the 860 cm^{-1} band exhibits a different dependence.

The cause of these dependencies can be traced to either of two effects, one of which is the influence of particle size and the other of which is due to changes in chemical composition. The following arguments can be involved in favor of the influence of composition.

a). Orthosilicates (SiO_4^{-4}) generally absorb at higher frequencies than do the corresponding metal silicates. Indeed, below are listed the positions for the corresponding bands for sodium orthsilicate and metasilicate, and the frequency differences the corresponding bands.

Sodium Orthosilicate (cm^{-1})	Sodium Metasilicate (cm^{-1})	Difference (cm^{-1})
1080	1020	60
990	950	40
920	870	50
840	795	45
755	700	55

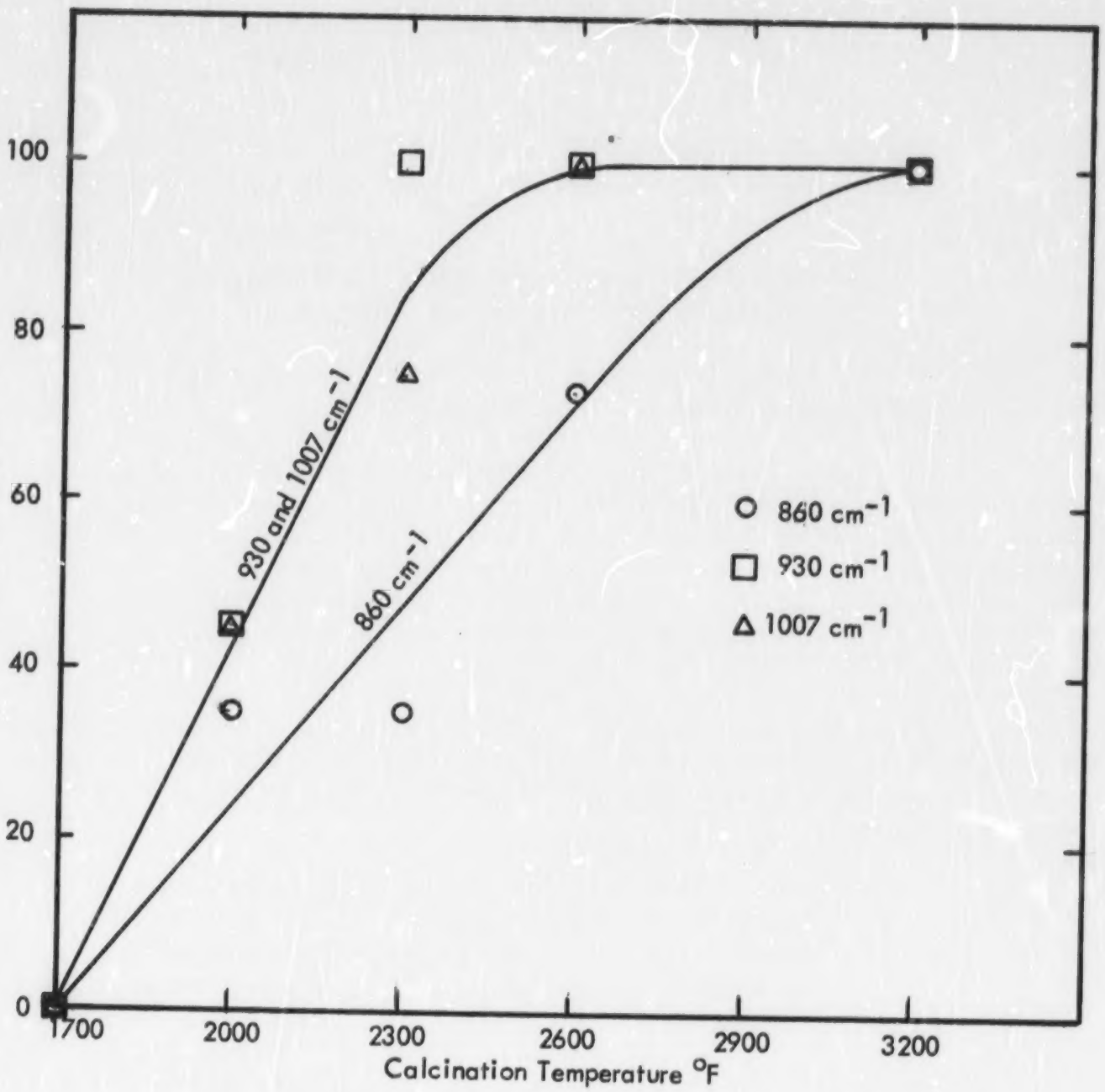

Figure 23. Percentage of Total Band Shifts Observed as a Function of Calcination Temperature

Thus, there is an average shift of ca. 50 cm^{-1} in going from Na_4SiO_4. The spectra of the two sodium silicates were run by the KBr pellet technique.

b). There is considerable evidence[21] that the reactions:

$$CaO + SiO_2 \longrightarrow CaSiO_3$$

$$CaSiO_3 + CaO \longrightarrow Ca_2SiO_4$$

do occur in limestones at the calcination temperature used in our work. Thus, our average shifts of ca 21 cm^{-1} could be readily explained by a partial reaction as the meta and orthosilicate bands, at least for the sodium salts, do overlap and the maximum positions would be expected to shift toward the orthosilicate positions as the reaction proceeded.

Further confirmation of the presence of meta and orthosilicates would require the use of other techniques such as X-ray diffraction. Such studies should, for ease of investigation, be conducted on samples of high silica content. It has not been possible to show, in this infrared study alone, where, with respect to the surface, the silicates are located. Indeed, our spectra were obtained by transmission and show only total silicates present. Evidence for or against preferential diffusion of silicates to the surface, as has been claimed[21] must be obtained by other techniques such as the use of the electron microprobe or low energy electron diffraction.

(b) Electron Microprobe Studies

Line analysis microprobe determinations for silicon content were run on a number of particles of the 1700°F and 3200°F calcined samples of the three series of samples provided by NAPCA. In addition, a small number of analyses were run for iron on the Series 102 samples, however insufficient data was collected for these runs to justify drawing any fair conclusions.

The experimental procedure consisted of making disk type samples in degassed epoxy resin; allowing the resin to cure and polishing of the disk until flat cross sections of a number of limestone particles were observed. Care was taken in these steps to avoid contamination of the surfaces with either silica or iron compounds. The disks were then taken and inserted into the microprobe apparatus and line scans across individual particle cross sections for silicon were run on a number of individual particles. A few similar runs were also made for iron.

Line scans across a number of individual particles of the 1700°F calcines of all three types of limestone for silicon revealed that almost all of the silica was confined to discrete regions of the particles. In an optical microscope these regions appeared to be darker and to constitute discrete phases. A typical line analysis run is shown in Figure 24

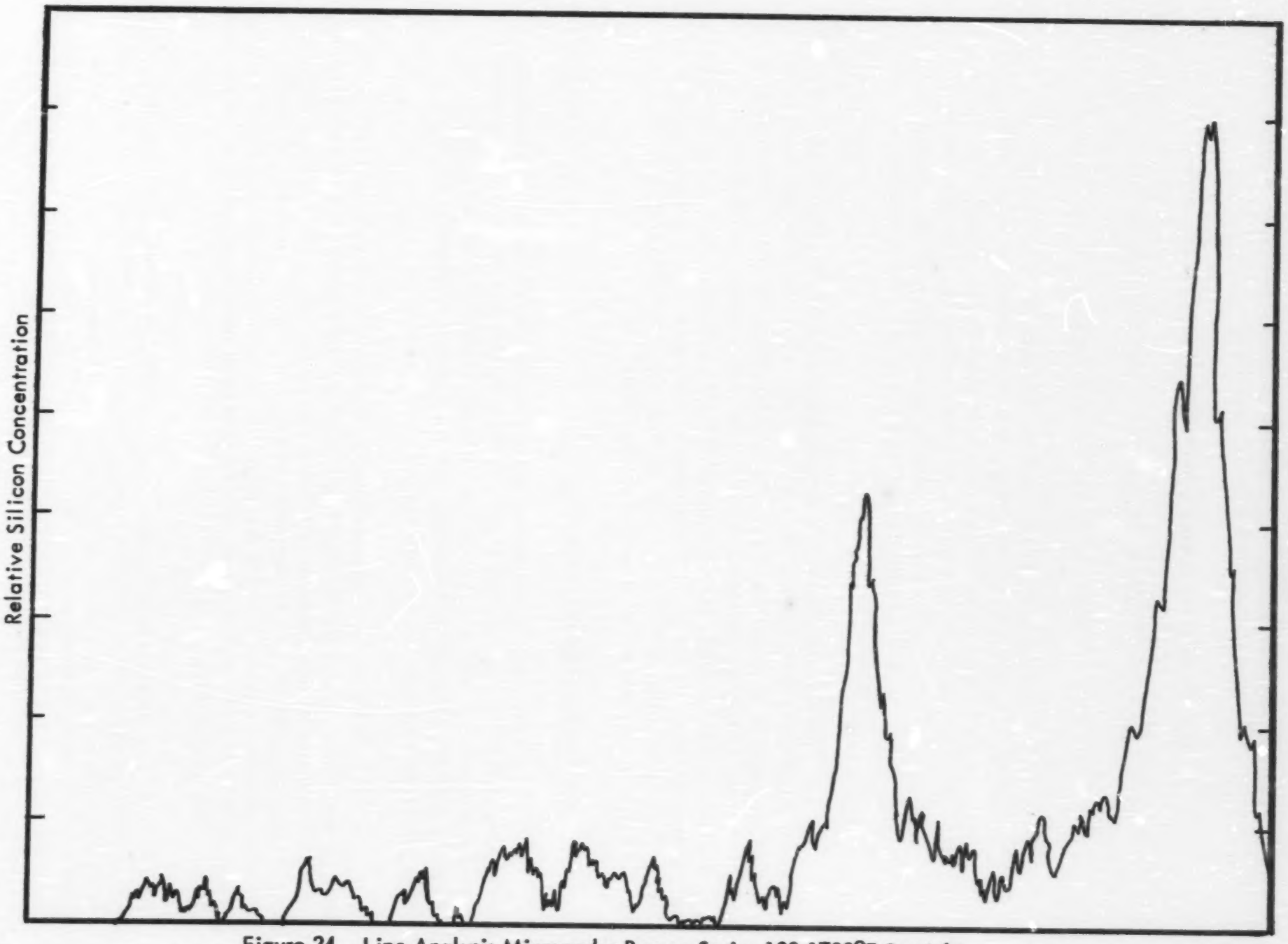

Figure 24. Line Analysis Microprobe Run on Series 100 1700°F Particle

for a 1700°F calcined particle of the Series 100 limestone. The trace was run across the particle at 160 μ/min. As can be seen, for the particle, most of the silicon was located in two small regions.

Similar scans were made on 3200°F calcines. A typical run is shown in Figure 25 for a Series 100 particle. As can be seen, while discrete regions of high silicon content are still present, most of the other material (or phases) present now also contain some silicon (i.e. silica has diffused throughout the limestone). This scan was made at 160 μ/min under the exact same conditions used for the 1700°F samples.

All of the above work can be taken as evidence for diffusion of silicates and possibly also for chemical reaction. Clearly, what is needed is a detailed analysis for calcium, oxygen and silicon for each of the phases (regions) present at different calcination temperatures to gain complete proof of the occurrence of chemical reactions. No enough particles were scanned during this brief study to gain much evidence for surface buildup of silicates. What is clearly needed in future work are microprobe scans for a number of elements run on a number of particles for different temperature calcines of each material. Only from such a collection of information can conclusive evidence for buildup of surface silicate layers be obtained. Also, the scanning rate in the above experiments was 160 μ/min. If the silicate layers are quite thin (i.e. ~1-2 μ), then a much slower scanning speed will have to be used to clearly detect their presence and composition.

(c) Studies of Hydration of Calcined Limestone

In a series of experiments pure magnesium and calcium oxides (Fisher Analytical Reagent grade) were exposed at 23°C to about 25 mm of water vapor in a vacuum system for a few hours. The water vapor was then removed by evacuation and the materials were then mixed with KBr. Pellets were then made and spectra were run. The results showed a sharp OH band at 3712 cm^{-1} for the hydrated MgO and a sharp peak at 3655 cm^{-1} for the calcium samples. The presence of these sharp OH stretching bands confirms the hydration of both CaO and MgO. For perfectly anhydrous samples, such bands were not observed. These experiments were repeated several times with the same results.

A number of uncalcined, calcined and reacted materials, provided by NAPCA, were also examined by the KBr technique. The behavior of the OH bands of many of these samples, both calcined and reacted, is presented in Table VIII. Those listed include all samples containing more than 5 percent MgO. For all other samples of this series examined, in all cases where less that 5 percent magnesium oxide was present, no band at 3712 cm^{-1} could be detected. As can be seen from the table, in all cases the 3712 cm^{-1} band appears to be removed by exposure to simulated flue gas at elevated temperature to a far greater amount than the 3650 cm^{-1} band is affected. Indeed, in many cases, while two bands were observed for the calcined samples, only one band, at 3650 cm^{-1}, could be detected for the reacted materials. A typical case is shown in Figure 26, where the top spectrum, of a calcined but unreacted material, containing 28 percent MgO, is shown to exhibit two strong bands at 3650 and 3710 cm^{-1}. The bottom

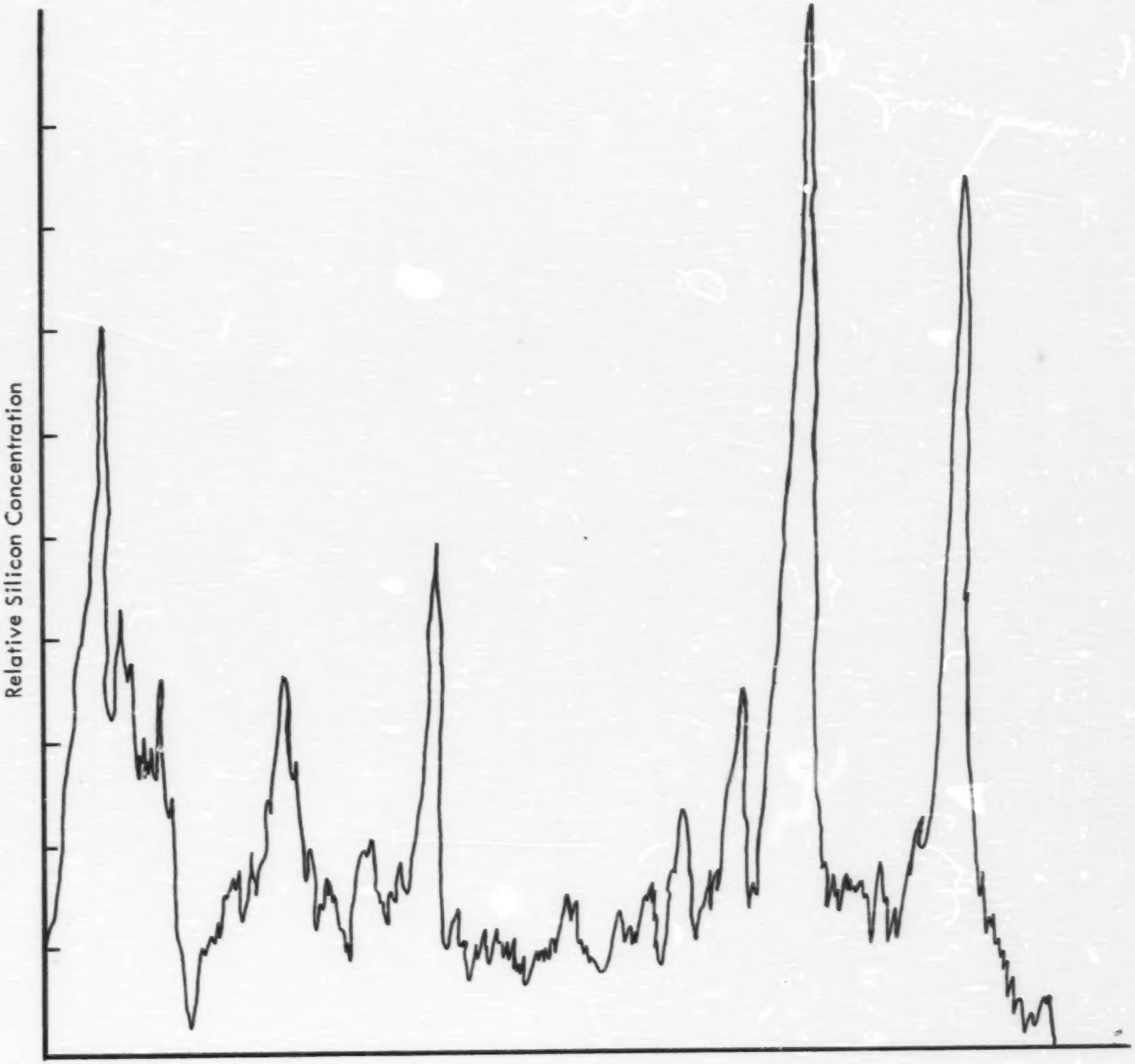

Figure 25. Electron Microprobe Line Scan for Silicon on 3200°F Series 100 Particle

Table VIII. Hydration of MgO and Evidence for Preferential Reaction Between MgO and Sulfur Dioxide

Sample Number	% MgO	Calcined	Reacted
200 BCR 1697	43	3712 cm^{-1} strong 3650 cm^{-1} strong	3712 cm^{-1} very weak 3650 cm^{-1} strong
201 BCR 1351	28.5	3712 cm^{-1} medium 3650 cm^{-1} strong	3712 cm^{-1} absent 3650 cm^{-1} strong
202 BCR 1352	31	3712 cm^{-1} medium 3650 cm^{-1} strong	3712 cm^{-1} absent 3650 cm^{-1} strong
203 BCR 1684	39	3712 cm^{-1} strong 3650 cm^{-1} strong	3712 cm^{-1} very weak 3650 cm^{-1} strong
204 BCR 1342	28	3712 cm^{-1} strong 3650 cm^{-1} strong	3712 cm^{-1} absent 3650 cm^{-1} strong
205 BCR 1361	7.2	3712 cm^{-1} very weak 3650 cm^{-1} strong	3712 cm^{-1} absent 3650 cm^{-1} strong
206 BCR 1360	13	3712 cm^{-1} weak 3650 cm^{-1} strong	3712 cm^{-1} absent 3650 cm^{-1} strong

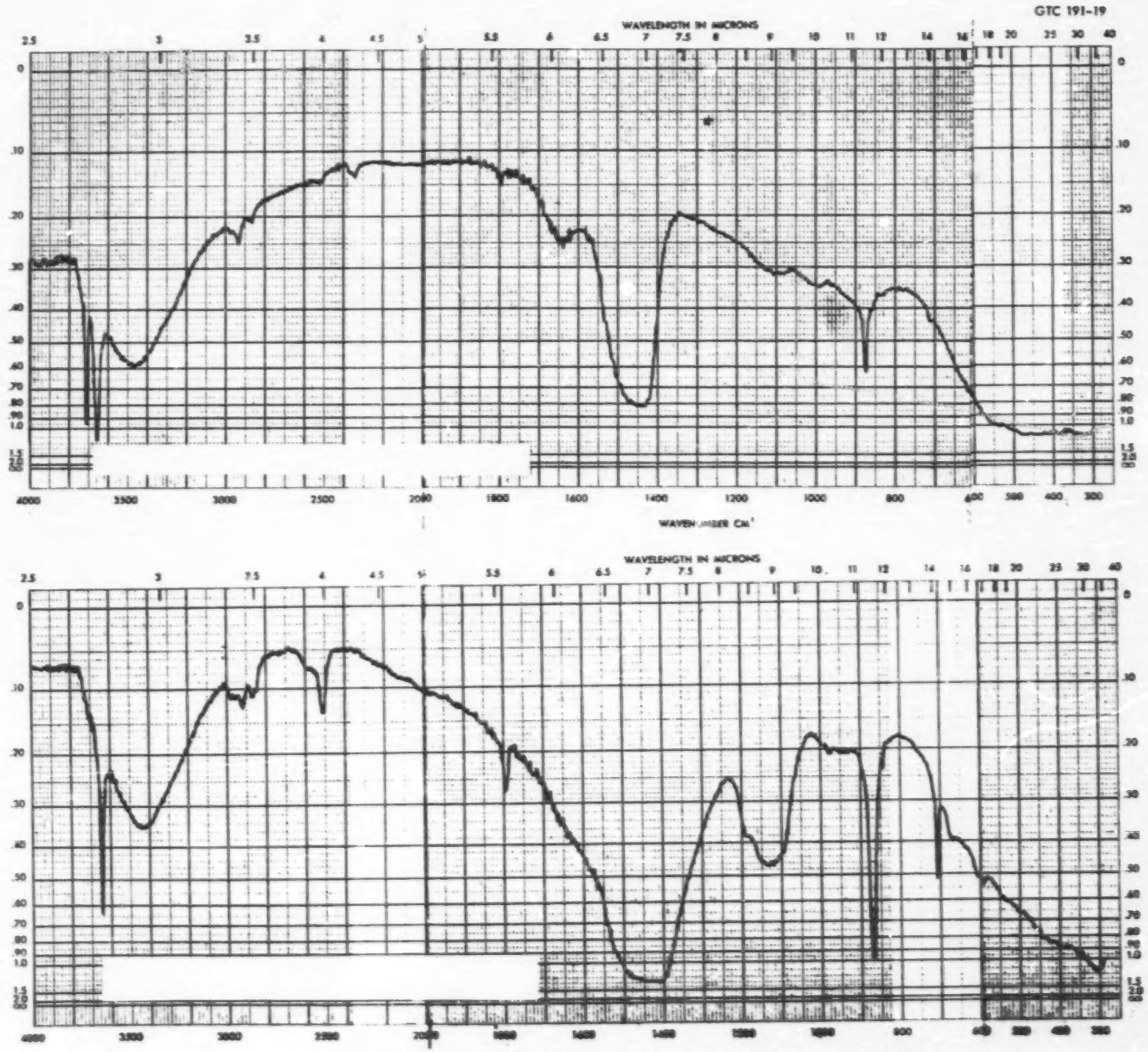

Figure 26. Preferential Reaction of Hydrated MgO with SO_2

spectra of this same material after reaction with flue gas, can be seen to exhibit only one OH band at 3650 cm-1. All of this may be taken as proof of the hydration of magnesium oxide in slaked dolomitic samples and of either a preferential reaction between MgO and some constituents of flue gases or a decomposition of magnesium hydroxide under reaction conditions.

C. HIGH TEMPERATURE KINETIC STUDIES

1. General Introduction

Work on an earlier program has shown that at fairly low temperature (i.e. ~250°C), the rate determining step in the reaction between calcined limestone, oxygen and sulfur dioxide is the oxidation of absorbed SO_2 (possibly as sulfite) to sulfate(4). Unfortunately, in these investigations, the individual steps in the overall process were not separately investigated and complete in situ reaction studies were not conducted using the infrared method. As a result, the conclusions drawn were somewhat open to question because the overall mechanism operating was not proven. The high temperature studies undertaken under this contract were performed to remedy the above information gaps and to obtain useful kinetic data at temperatures closer to those used under operating process conditions.

2. Experimental

For all of these investigations, a set of high temperature optical cells were used. The sample cell, as is shown in Figure 27 contained NRC foil flanges capable of withstanding repeated heating and cooling cycles from cryogenic temperatures to over 500°C. The cell body was made of stainless steel and aluminum gaskets were used to achieve an airtight seal between the detachable parts. The exit and entrance gas ports contained Kovar seals for attachment to glass apparatus.

As it proved impossible to obtain a sealant with which to attach the Irtran 2 windows to the cell, another approach was used. The windows were of a size that they fitted reasonably tight into their position. The insertion of tight fitting metal large "O" ring type spacers behind these windows were found to hold them quite firmly in place. While such a system was not vacuum tight, outgassing of the samples plated onto the windows could still be accomplished in a stream of flowing inert gas at elevated temperatures. A sketch of this part of the system is shown in Figure 28. Also, as the windows were tight fitting and the exit gas port from cell was fairly large in cross-sectional area, gas losses around the windows were expected to total no more than one or two percent (from cross-sectional area considerations) of the total gas flow. As the sample was exposed to a constant flowing stream of gas, contamination back diffusion through small window leaks was shown to be negligible.

For the reference beam cells, a high temperature single cell(4), minus its Viton "O" rings, was used. In this state this cell could be maintained at the same temperature as the working cell, but could not be evacuated. This cell contained an

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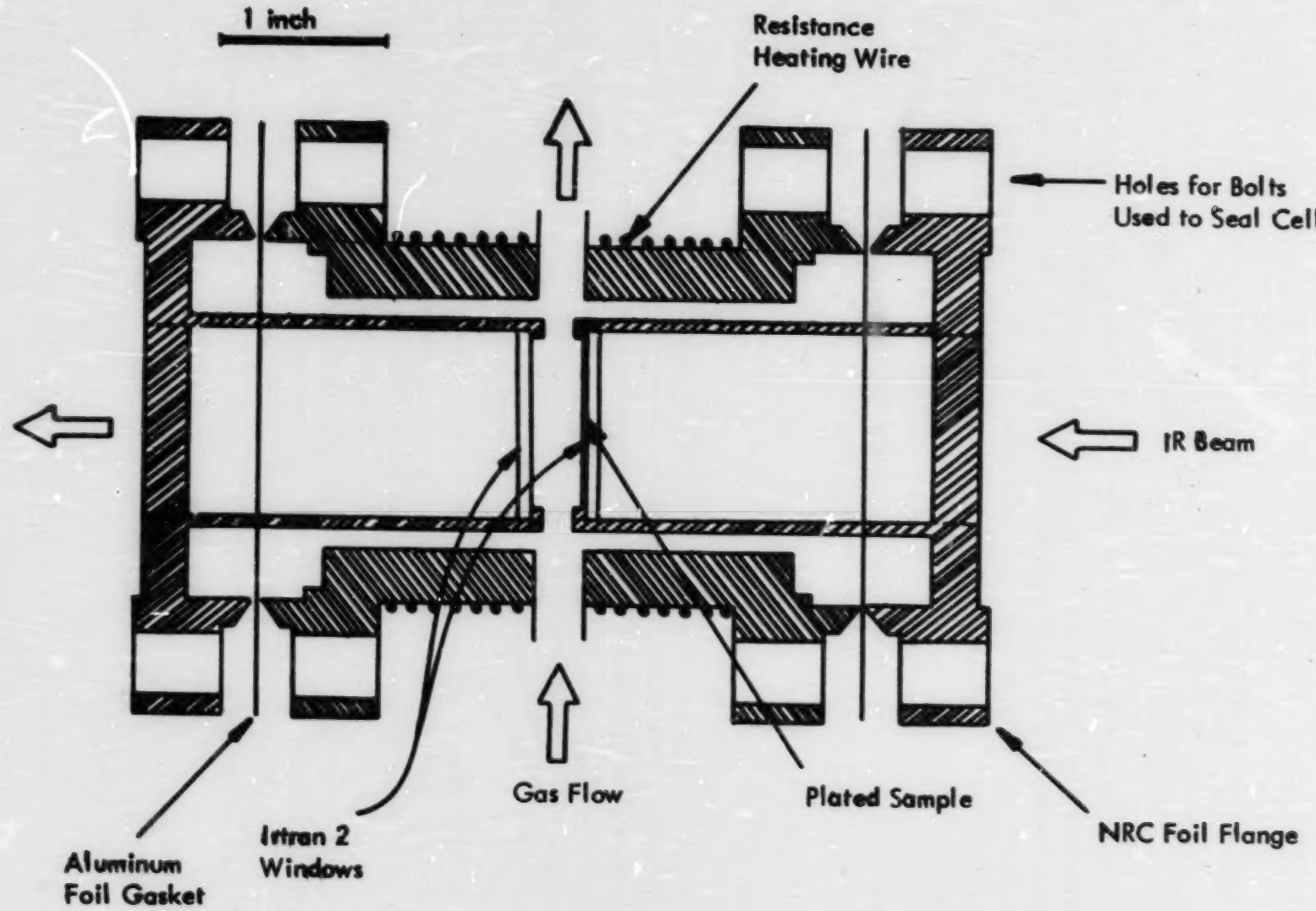

Figure 27. Design of High Temperature Cell for Use in Dual Cell System

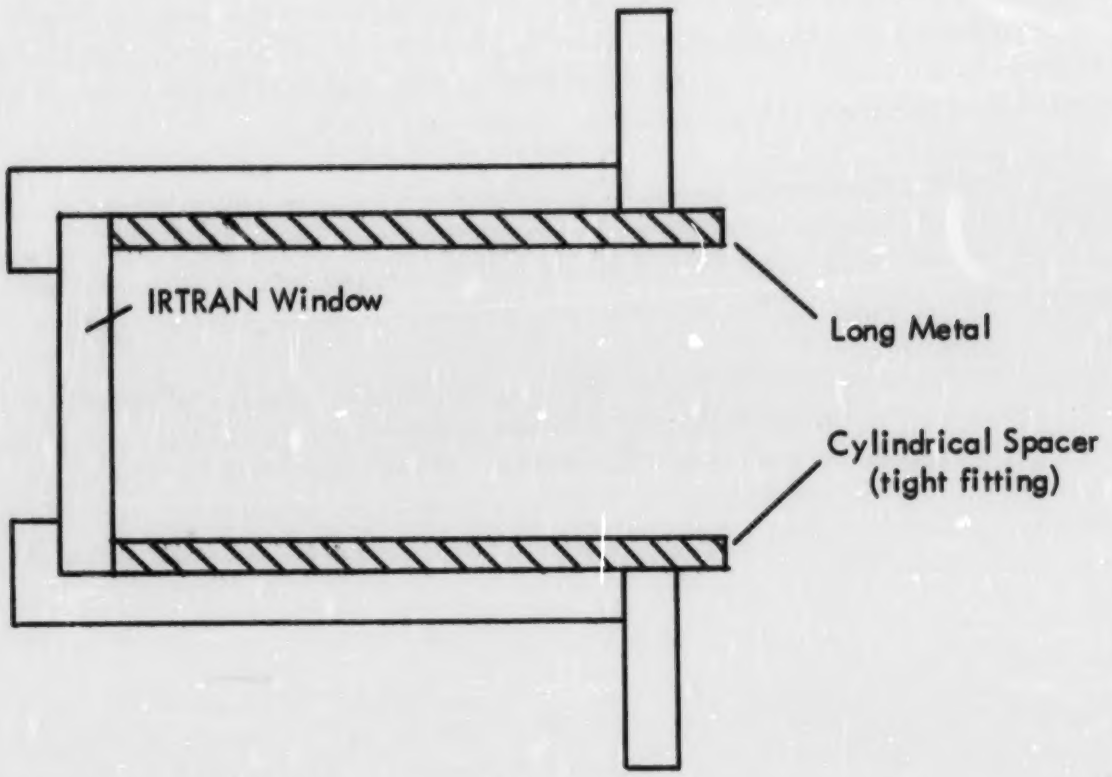

Figure 28. Diagram of System Employed to Hold Windows in Place

identical set of Irtran 2 windows and for all experiments was maintained at the same temperature as the sample cell to minimize radiation problems. No gases were flowed through the reference beam cell.

For the high temperature studies, samples were deposited on the Irtran windows by spraying a suspension of limestone in acetone onto the windows and allowing the acetone to evaporate. Prior to conducting all of the runs, the samples were outgassed at the run temperature in nitrogen at 400°C. The limestone used in all of the studies was the 1700°F calcined Series 100 material provided by NAPCA. The total sample weight on both windows was kept at ca. 50 mg for all experiments. Some problems initially encountered in these studies with variation in flow rates were solved by placing a flowmeter at the exit of the cell. Temperatures were maintained by the insulated resistance wire heater around the cells. Temperatures, which were monitored by thermocouples attached to the windows, could be readily maintained at ± ca. 5°C for all experiments. All gases were fed into the cells from a gas mixing system described in an earlier study[4]. Each of the gases was fed from its tank source, through a calibrated flow meter, into the flow lines, the N_2 was presaturated by two water presaturators in series at 22°C.

In all experiments, the windows plus samples were carefully weighed before and after reactions with SO_2 to gain the weight increases (and hence amount of product formed). This information was used to compute kinetic data presented later in this report. The surface area of the Series 100 limestone used was 3.1 m^2/gm.

In these studies, 475°C was the highest temperature investigated. Efforts were made to gather information at higher temperatures due to problems involving window oxidation and degradation under such conditions. It was found that at 500°C, a small amount of window oxidation occurred. For more data to be obtained at such elevated temperatures, a window material more resistant than Irtran 2 would have to be used.

3. Results

Preliminary scans run on samples during reaction between limestone (Fredonia 1700°F) and a simulated flue gas consisting of 0.3% SO_2, 2% O_2, 2% H_2O, and the balance nitrogen revealed formation of both sulfite and sulfate at 400°C. The sulfite and sulfate band maximum were seen at 920 and 1110 cm^{-1}, respectively. No bands due to sulfate or sulfite formation could be detected by passing the flue gas through the empty cell past the Irtran 2 windows.

During these studies, it was found that the band intensities increased markedly in cooling of the sample to room temperature. Accordingly, an experiment was performed with a reacted sample, wherein the sample beam runs blocked off and the emission spectra of the 400°C sample was recorded. The spectra clearly showed emission bands at 1110 and 920 cm^{-1} due to sulfate and sulfite. As the intensity of the emission bands were expected to increase with rising temperature, the absorbances of samples should decrease with increasing temperature for our present arrangement. This did not prove to be a problem at the temperatures of our study, but probably would cause severe problems at more elevated temperatures.

Using the apparatus (i.e. the dual cell with the reference cell consisting of two Irtran 2 windows maintained at the same temperature as the sample cell), kinetic experiments were performed in the 380-475°C range. In one study, a mixture of 0.3% SO_2, 2% water vapor, balance nitrogen was passed over the samples at 800 cc/min and the 920 cm^{-1} absorbance was monitored with time using the external recorder. Gas flow rates were monitored at room temperature. The absorbances were found to increase with time in a semi-logarithmic manner in all cases, leveling off to a fixed value after finite times. A kinetic plot of one of these experiments is presented in Figure 29. The vertical scale,

$$1 - \frac{\text{absorbance - initial absorbance}}{\text{total absorbance change}}$$

can be shown by simple algebra to be equivalent to

$$\frac{1 - \text{const. conc. } SO_3^{=}{}_T}{\text{const. conc. } SO_3^{=} \text{ final}}$$

where conc. $SO_3^{=}{}_T$ is the concentration of $SO_3^{=}$ at time T and conc. $SO_3^{=}$ final is the final concentration of $SO_3^{=}$, which was the concentration of sulfate present when no further absorbance changes occurred at 920 cm^{-1}.

Now, $KSO_3^{=}$ final is proportional to the total number of reactive sites (i.e. to the total amount of reactive CaO. Thus, $KSO_3^{=} - KSO_3^{=}{}_T$ is proportional to the amount of unreacted CaO at time T. Therefore, the above expression becomes:

$$\frac{\text{conc. unreacted } CaO_T}{\text{CaO reactive Total}}$$

and the vertical axis of Figure 29 may be expressed as log conc. CaO. The linearity this plot (Figure 29) is of interest in that it demonstrates a first order dependence on CaO concentration for the reaction:

$$CaO + SO_2 \longrightarrow CaSO_3$$

Another series of experiments were conducted monitoring the sulfate band at 1110 cm^{-1}. In one series of experiments, the absorbance at 1110 cm^{-1} was monitored with time and in the other series of experiments, scans were made at ten minute intervals between 1300 and 800 cm^{-1}. These runs were all conducted between 380 and 450°C using a gas mixture consisting of 0.3% SO_2, 2% water, 2% oxygen and the balance nitrogen. The flow rates for all these runs were 800 cc/min. Plots of

$$\frac{1 - \text{absorbance}_T - \text{initial absorbance}}{\text{Total absorbance change}}$$

versus time are shown for the 1110 cm^{-1} sulfate band for one run in Figure 30. As can be

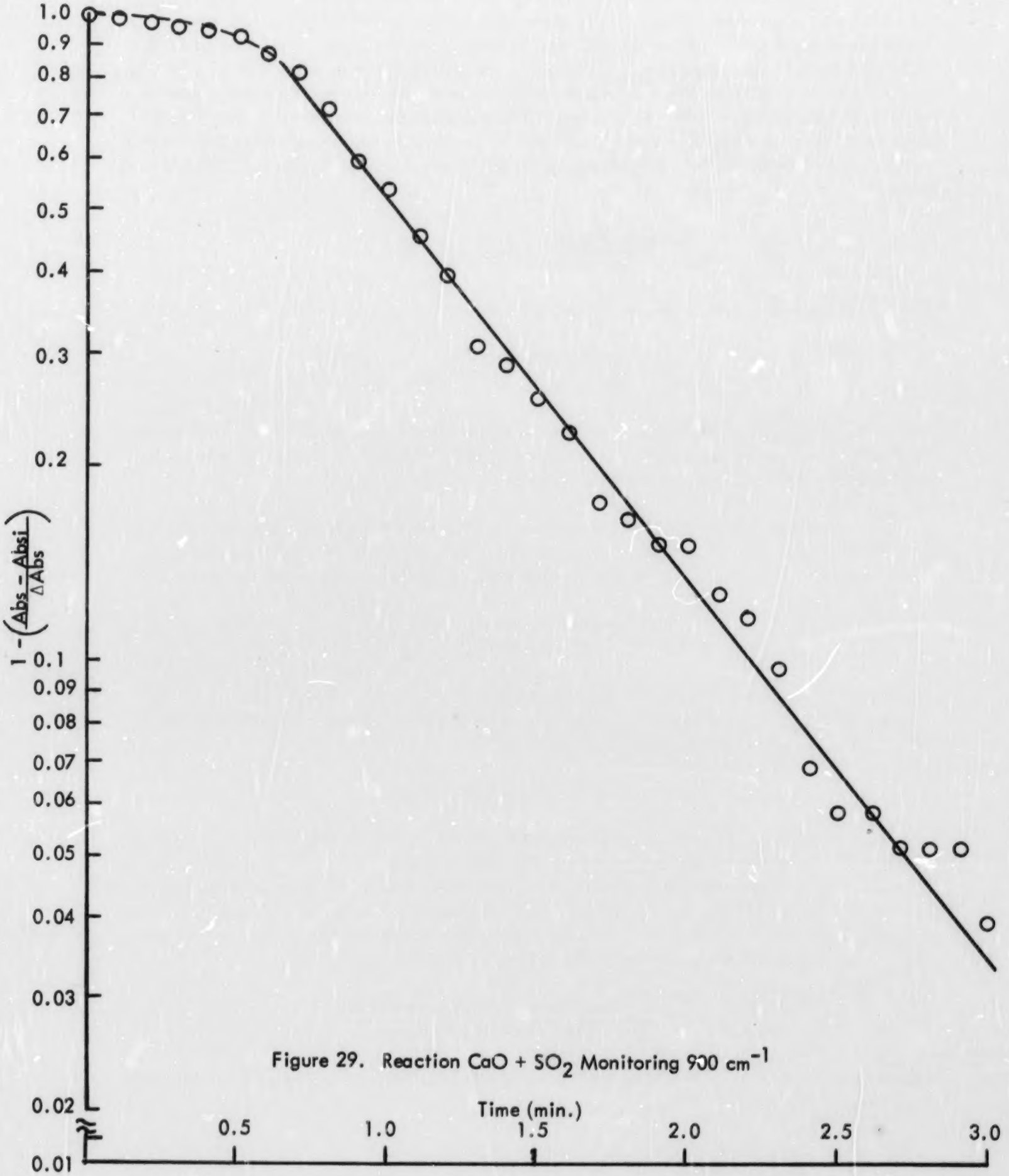

Figure 29. Reaction CaO + SO_2 Monitoring 900 cm^{-1}

12/18 - scans

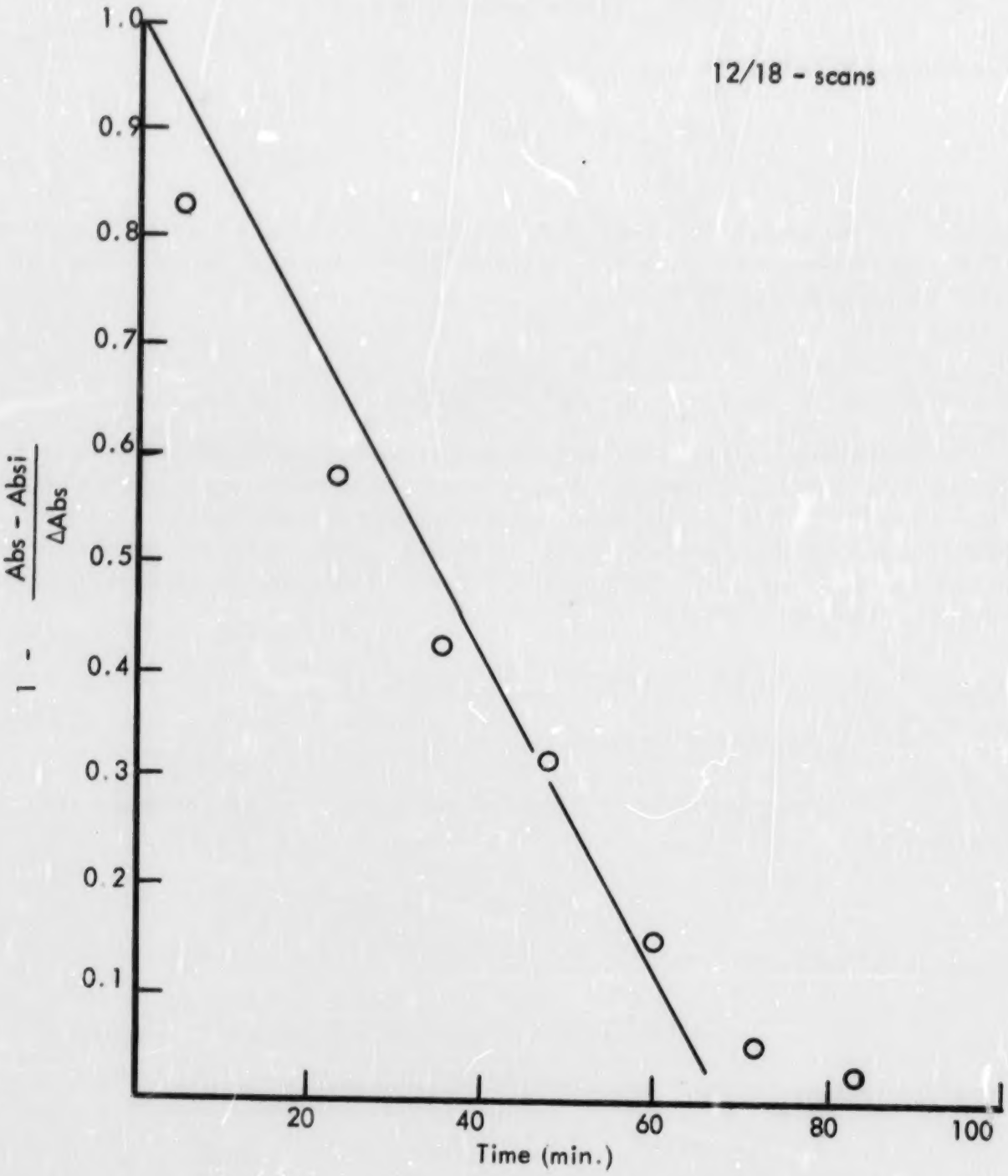

Figure 30. Reaction $CaO + SO_2 + 1/2O_2$ Monitoring 1110 cm^{-1}

seen, for conversion to sulfate, a zero order kinetic process appears to be operating. The

$$\frac{1 - \text{absorbance}_T - \text{absorbance initial}}{\text{Total absorbance change}}$$

can be shown to be related to both:

$$\frac{1 - KSO_4^{=}{}_t}{KSO_4^{=}{}_F} \qquad \text{and} \qquad \frac{KSO_4^{=}{}_F - KSO_4^{=}{}_T}{KSO_4^{=}{}_F}$$

where $SO_4^{=}{}_t$ is the concentration of sulfate at time T and $SO_4^{=}{}_F$ is the final concentration of sulfate achievable. Now, as $SO_4^{=}{}_F$ is related to the amount of reactable CaO initially present, the above can be rewritten as

$$\frac{K\,CaO_T}{K\,CaO_{\text{total reactable}}}$$

Thus, the zero order kinetics reveals that the rate of conversion to sulfate is independent of the concentration of CaO present. This zero order dependence was exhibited for all of the runs monitoring 1110 cm^{-1}. Also, good agreement was obtained between both methods of monitoring absorbance changes. In all the studies, complete conversions to sulfate were not achieved, as judged by weight gains. In most cases, about 40 percent of the CaO present was reactable.

4. Discussion of High Temperature Study Results

(a) Mechanism of Reaction

The experiments performed have shown a first order dependence in CaO for the reaction:

$$CaO + SO_2 \longrightarrow CaSO_3$$

and a zero order dependence for:

$$CaO + SO_2 + 1/2O_2 \longrightarrow CaSO_4$$

This can be interpreted in terms of the following mechanistic sequence

1. $CaO + SO_2 \longrightarrow CaSO_3$ (fast)
2. $CaSO_3 + 1/2O_2 \longrightarrow CaSO_4$ (slow)

As reaction 1 is far more rapid, the surface becomes rapidly covered by sulfite, which is only slowly converted to sulfate. Such a scheme would readily explain the observed kinetic dependences.

Relevant rate data extracted from the series of curves obtained monitoring 1110 cm^{-1} is presented in Table IX. A plot of this data appears in Figure 31. From this plot of rate versus reciprocal temperature, an activation energy of 41.9 Kcal is computed for the oxidation reaction resulting in sulfate formation. A similar data evaluation was conducted for the information obtained monitoring the 920 cm^{-1} sulfite band. Table X gives the rate data obtained from these runs and a plot of this data is also presented in Figure 31. From this graph of rate versus reciprocal temperature, an activation energy of 13.9 Kcal/mole was computed for the SO_2 absorption reaction (step 1).

The rate data presented here clearly shows that at temperature below ~500°C, the rate of oxidation of sulfite

$$(\text{i.e. } CaSO_3 + 1/2O_2 \longrightarrow CaSO_4)$$

is the rate determining reaction. Above 500°C by extrapolation of the data, such as can be seen from Figure 31, the rate of absorption of SO_2 becomes rate determining. Indeed, the activation energy we are reporting for this step (13.8 Kcal/mole) agrees well with the overall activation energies reported for the dry limestone process at higher temperatures (ca. 900°C). Values ranging from 8 to 18 Kcal/mole have been reported at these temperatures(11).

Table IX. Rate Data for the Reaction $CaO + SO_2 + 1/2O_2 \rightarrow CaSO_4$

Temperature (°C)	Time for Complete Reaction		Molecules/cm^2 sec	$1/T \times 10^3$
	Minutes	Seconds		
400	63	3.78×10^3	3.08×10^{12}	1.50
400	65	3.90×10^3	2.97×10^{12}	1.50
380	110	6.6×10^3	1.97×10^{12}	1.5
450	6.5	3.9×10^2	3.00×10^{13}	1.3
445	8.3	4.3×10^2	2.61×10^{13}	1.39

Table X. Kinetic Data of SO_2 Absorption

Temperature	Time (sec)	$\frac{1}{T} \times 10^3\ {}^oK^{-1}$	Molecules (cm^2 sec)
400	372	1.50	3.12×10^{13}
420	318	1.44	3.65×10^{13}
450	204	1.38	5.70×10^{13}
408	264	1.48	4.40×10^{13}
475	144	1.34	8.05×10^{13}

It has been reported at higher temperatures that the overall absorption and oxidation rate of SO_2 is dependent in first order on the SO_2 concentration(11). This finding strongly supports the above conclusions. Indeed, from the above we are postulating

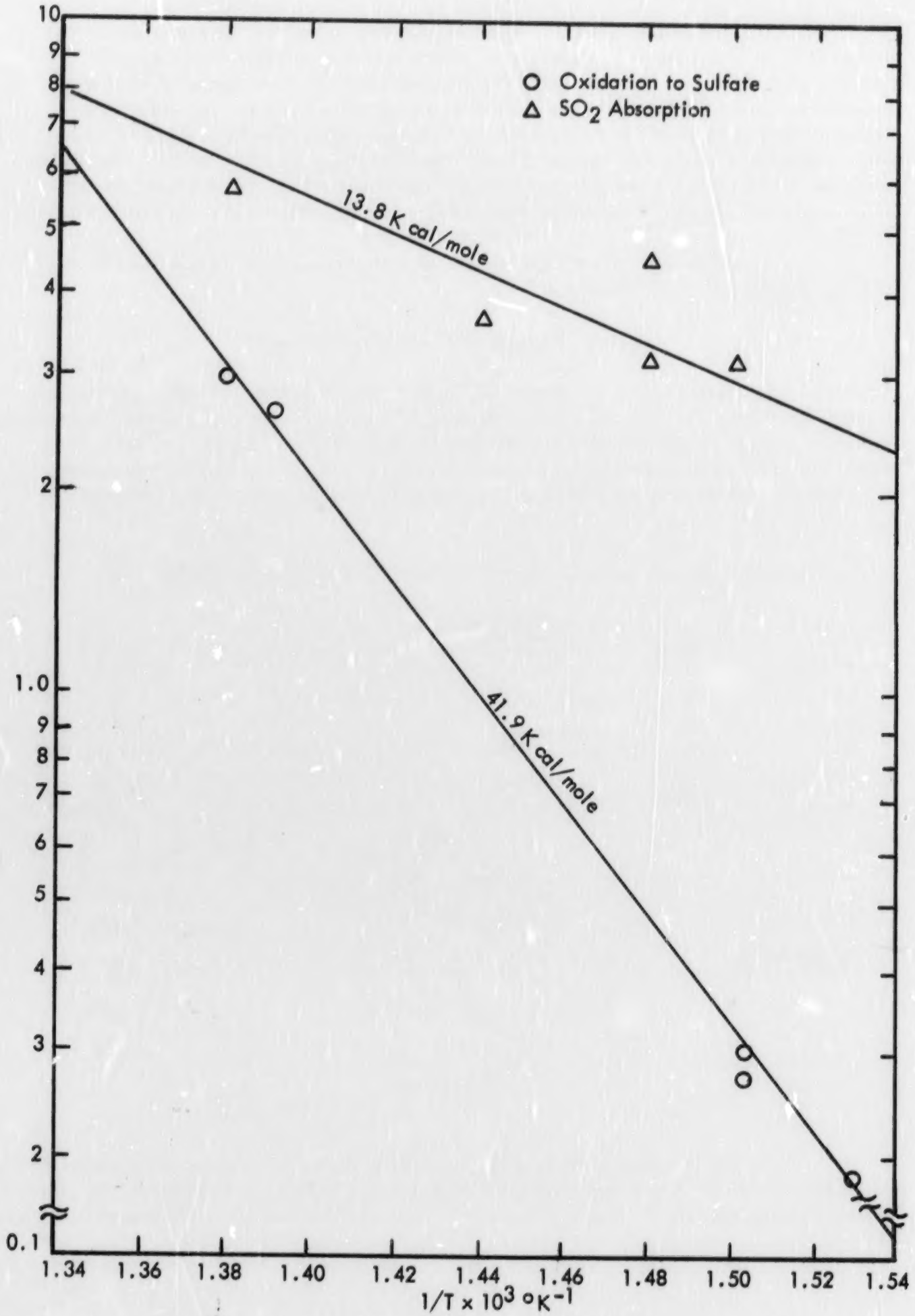

Figure 31. Kinetic Plots of Data for SO_2 Absorption and Oxidation Steps

as the rate determining reaction at elevated temperatures

$$CaO + SO_2 \longrightarrow CaSO_3$$

Such a reaction is expected to be first order in both CaO surface concentrations and in SO_2.

(b) Calculation of Pre-Exponential Factors for the Absorption and Oxidation Steps

(1) Oxidation of Sulfite to Sulfate

Using the equation $A = A_o e^{-\Delta H^*/RT}$, where A is the number of molecules/site sec at a given temperature, A_o is the pre-exponential factor, ΔH^* is the activation energy, R is the gas constant and T the absolute temperature, and rearranging, we have:

$$A_o = A\, e^{\Delta H^*/RT}$$

Using the 450°C data presented in Table IX for sulfate formation, we have, assuming 10^{-15} cm^2/site (i.e. each site = 10 $Å^2$):

$$Ao = 3 \times 10^{-2} \text{ molecules/site sec } e^{\frac{41,900}{2(723)}}$$

$$Ao = 9.51 \times 10^{10} \text{ molecules/site second}$$

$$= 9.51 \times 10^{25} \text{ molecules/cm}^2 \text{ sec}$$

$$= 1.58 \times 10^{2} \text{ moles/cm}^2 \text{ sec}$$

(2) Absorption of SO_2

Using the same equations above and data presented in Table X we have:

$$Ao = 5.7 \times 10^{-2}\, e^{\frac{13,800}{2(723)}}$$

$$= 7.07 \times 10^{2} \text{ molecules/site sec}$$

$$= 7.07 \times 10^{17} \text{ molecules/cm}^2 \text{ sec}$$

$$Ao = 1.18 \times 10^{-6} \text{ moles/cm}^2 \text{ sec}$$

A comparison of the above Ao values with each other clearly demonstrates what was stated earlier in this report (i.e. that at temperatures at which the dry limestone process is operated (900°C) the absorption of SO_2 is clearly the overall

rate limiting step. Indeed, a surface reaction of the type $CaO + SO_2 \rightarrow CaSO_3$ would be expected to be first order in both reactants. While time did not allow us to fully confirm this point on this program, a few experiments could really check the overall validity of the above postulated kinetic picture. Rates could be measured at several SO_2 partial pressures using the Series 100 materials. All of these runs, of course, would be conducted at the same temperature. Also, data obtained by monitoring the rate of sulfate formation at 1110 cm^{-1} taken above 500°C should prove most revealing when correlated with data obtained above. Indeed, if SO_2 absorption is rate limiting, then the rate curve for sulfate formation (Figure 31) should exhibit a bend and follow the same line as the SO_2 absorption curve as, for our experiments, sulfate cannot be formed faster than SO_2 is absorbed. Indeed, if SO_2 absorption is rate limiting and the rate of oxidation to sulfate is much faster than the absorption reaction (as is expected to be the case above 500°C), then the rates of SO_2 absorption (as determined by the formation of the 920 cm^{-1} band in the absence of O_2) should be the same. These points could readily be checked to give a complete proof of the mechanism postulated in this report.

SECTION III

CONCLUSIONS AND RECOMMENDATIONS

This study has illustrated the applicability of infrared methods to the study of problems involved in various limestone scrubbing processes. Using infrared spectroscopy it has been possible to show the mechanism by which limestone removes SO_2 from flue gases in the presence of oxygen, to demonstrate that high temperature reactions with silica or silicates occur in impure limestone during calcination, and to develop a rapid method for analysis of the sulfate content of reacted limestone which may be extendable to analysis for other species of interest as well.

The results of this program may be summarized as follows:

1. Pressed pellet techniques, either when used alone as in conjunction with freeze drying and ion exchange methods, do not give as precise results as can be achieved by wet chemical means. The pressed pellet method alone gives calibration curves which contain considerable scatter. When used with freeze drying techniques, the pellet method can give good results, but the process becomes very time consuming. Application of ion exchange techniques does, apparently, lead, in conjunction with the pellet technique, to a reliable method for sulfate analysis, but this approach cannot be extended without great difficulty to analysis for carbonate and hydroxide.

2. A new type of thin film cell has been developed which will allow investigators to make quantitative studies in water based solvent systems by infrared methods. The new cell, .003 mm thick consists of two optically flat silver chloride plates. On the outer portions of the face of one of these plates is deposited a uniform 3 micron silver film.

3. Studies using a matched pair of such cells (one containing the water based solvent which was placed in the reference beam and the other containing test solutions, which was inserted in the sample beam) have shown that, using saturated tetrasodium EDTA aqueous solution as a solvent and a differential technique, quantitative analysis of the sulfate contents of reacted limestone can be readily conducted.

4. Investigations have shown that the techniques developed for sulfate analysis in solution can be extended to studies of species such as carbonate, nitrate, nitrite, dissolvable silicate, and phosphate. If D_2O is used in place of water as the solvent, then such techniques may also be extendable to hydroxide and oxide.

5. Studies, using the KBr technique, have shown that shifts and changes in intensity per unit weight of sample occur for the silicate bands in

impure limestones with increasing calcination temperature. This evidence can be correlated with data on different kinds of silicates and it can be demonstrated that reactions are occurring with silica or silicates within the impure limestones during calcination at higher temperatures. Some electron microprobe data obtained on the same materials as were used for the infrared studies has revealed that after calcination at low temperatures (1700°F) essentially all the silicates are present in discrete phases within the limestones. After calcination at higher temperatures (3200°F) some silicate is present in all phases of the limestone.

6. The hydration of MgO in calcined, slaked dolomitic materials has been confirmed and evidence has been obtained to indicate either a preferential reaction of the hydrated MgO with some flue gas constituent or a decomposition of $Mg(OH)_2$ under conditions of reaction of dolomites with flue gases.

7. Infrared studies of the reaction of SO_2 with limestone in the 380-475°C temperature range have provided a large volume of useful kinetic data. It has been demonstrated that the absorption reaction, $CaO + SO_2 \longrightarrow CaSO_3$, with an activation energy of 13.8 Kcal/mole is the rate determining reaction above 500°C. At lower temperatures, the oxidations reaction, $CaSO_3 + 1/2O_2 \longrightarrow CaSO_4$, with an activation energy of 41.9 Kcal/mole is rate determining. Pre-exponential factors have also been obtained for the above reactions.

To further utilize the techniques developed in this study and to gain further needed information by infrared methods on some of the problems involved in limestone scrubbing processes, the following set of recommendations are made:

1. Thin film type cells of the variety used in the development of the method for sulfate analyses should be developed from more resistant materials than silver and silver chloride. An investigation should be made of other window and film materials to determine the best combinations of useable compounds. Specifically, materials such as zinc sulfate, zinc selenide, silicon, KRS-S, germanium and arsenic trisulfide glasses, which are known to be water resistant should be investigated for use as possible window materials to be used with the alkaline (pH ~9) EDTA solutions. A study should also be made of the use of thin films of materials such as Teflon and tantalum, which are both corrosion and wear resistant, for use as films or spacers.

2. The design of the thin film cells used in this study, while novel, presented some difficulties. With the thickness of the cells being only 3 microns, however, problems have been encountered in filling of these cells. In future work, studies should be made with the aim of developing a more readily fillable cell. One possible approach to this problem lies in the design of an evacuable cell, where the test solutions can be drawn into and through the cells via evacuation.

3. The methods and techniques developed for rapid analysis of sulfate in an aqueous based solution should be extended to development of procedures for rapid analyses for species such as nitrate, nitrite, carbonate, bicarbonate, sulfite, and bisulfite. Efforts should be made to determine which of these species and sulfate can be determined in the presence of one another in solution. Perhaps, it may be possible, from one spectrum, to determine the concentrations of several species of interest.

4. Work with the methods developed for sulfate analysis should be extended to the use of D_2O based solutions. In such solutions, it may be possible to conduct analyses for species such as oxide and hydroxide.

5. Should work conducted along the lines suggested by the above four recommendations prove promising, a study should be made of the feasibility of producing thin film cells of the type developed for general use along the lines suggested by the earlier recommendations.

6. The studies of deadburning should be extended to include the following:

   a. On a number of series of well-defined samples, infrared and microprobe studies should be conducted to determine the silicate and iron distributions as a function of calcination temperature. Each of the series of samples should have a high content of only one impurity and should be fairly free of others. This will make interpretation of the results much easier. All samples for these studies should be handled under enert atmosphere to prevent unwanted reactions with CO_2 and water vapor.

   b. A series of detailed chemical analyses via the microprobe technique would be conducted on several particles of each of the limestone materials to be studied. The calcium, silicon (or iron) and oxygen content of each of the phases present in the particles should be determined as a function of calcination temperature. This information, coupled with the infrared spectra to be obtained, should lead directly to a knowledge of which silicates are present at different calcination temperatures.

7. The high temperature kinetic studies should be extended to include the following:

   a. An investigation of the kinetic dependence upon SO_2 partial pressure of the rates of sulfate and sulfite formation.

   b. A study, at fixed SO_2 partial pressure, of the rates of sulfate and sulfite formation at temperatures above 500°C.

c. Volumetric experiments to determine the rate of SO_2 absorption at various SO_2 partial pressures in the same temperature range as the kinetic studies presented in this report. This additional data will provide enough information to either prove or disprove the mechanisms proposed in this report.

SECTION IV

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SECTION V

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